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Surface mineral analysis from two possible Martian analogs (Rio Tinto and Jaroso Ravine, Spain) using micro-, macro-, and remote laser Raman spectroscopy

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The analysis of the geological context in which a series of minerals are formed is relevant in terms of the reconstruction of the geological history of Mars and also in terms of its potentiality to be used as appropriate targets in which a more close inspection about possible signs of past or present life can be performed.

Among the different techniques for in-situ analysis of minerals and possible biomarkers in robotics planetary missions the combination of Raman and LIBS are of particular importance. LIBS is a powerful technique for elemental chemical identification and quantification while Raman is very useful for analytical identification of molecular species.

In the context of the design and development of an integrated Raman-LIBS instrument (EXLIBRIS)[1] for EXOMARS program detailed test of each technique need to be performed separately in both laboratory and field analysis.

The aims of the present work is to show the methodology developed for in-situ surface analysis of minerals using Raman spectroscopy. Such type of analysis represent a first step in the whole of the work and must be followed by consecutive work with the integrated LIBS-Raman system including biomarkers.

These studies have been performed in two areas of South Spain which are relevant as possible Martian analogs, Rio Tinto and Jaroso Ravine. Rio Tinto (Huelva province) is an evaporitic system that represent an important analogue to searching for life in highly acidic liquid water, deep beneath the subsurface of Mars [2]. Jaroso Ravine is an hydrothermal system located at Sierra Almagrera, Almería province which is the world type locality of jarosite [3].

Both are perfect candidates to carry out a mineralogical comparative study of oxide, hydroxide and sulphate minerals, in particular those belonging to the jarosite-alunite group.

Raman spectra were taken in three different modes micro-, macro- and remote mode using three different portable spectrometers.

A HoloLab 5000 Raman spectrometer from Kaiser Optical Inc. illuminated with two different laser wavelengths, 632.8nm from an He-Ne laser and 532nm from a second harmonic Nd:YAG laser. A SPEX 270M Raman spectrometer illuminated with the 514.5 nm of an Ar^+ ion laser and a HE Raman spectrometer from Jobin Yvon Inc. illuminated with the 785nm wavelength of a diode laser.

Objectives of 20x and 100x magnification and 50x long working distance were used in micro mode. In macro mode several Raman probe head were tested from Kaiser Optical System, Yobin Ivon Inc. and InPhotonics with working distances ranging from 15 to 45 mm. In remote mode two Raman spectrometers were coupled to a Meade ETX telescope an spectra were performed in the range 9 to 20 meters using 541.5 and 632.8 nm excitations.

Samples with different sizes ranging from several millimeters to a dozen of centimeters were analyzed without any preparation.

Several real conditions were also tested: laser power limits of detection, in-focus and out of focus conditions as well as different ambient light conditions in the measurements performed in field analysis and in remote mode.

Spectral data were automatically treated using a software package developed within our group. These treatment comprises base-line corrections, signal to noise improvement, self-deconvolution and band fitting and finally automatic mineral identification using our standard database.

Micro and macro Raman spectroscopy were able to identify unambiguously mineral phases in most of cases including silicates, oxides, hydroxides and sulphates. In this last case a great variety of iron bearing sulphates were identified in both locations.

Rio Tinto shows mainly rhomboclase, coquimbite, rozenite and copiapite minerals.

In the Jaroso Ravine alunite minerals are the most abundant including jarosite and natrojarosite. Hallotrichite, kalinite, gypsum and barite were also identified.

The results obtained have been analysed and discussed on the basis of the different mineralization context in both Tio Tinto and Jaroso Ravine.

These results stressed the capabilities of Raman spectroscopy to identify specific minerals and also the potential applications of the technique for in-situ mineral identification in future robotic missions to Mars.

References

1. EXLIBRIS proposal (EXomars Laser Induced Breakdown-Raman Integrated Spectrometers) is an ongoing project to develop a compact set of a Laser Induced Breakdown Spectrometer (LIBS) and a Raman spectrometer for Pasteur payload.

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