# SURFACE-ENHANCED RAMAN MICRO-SPECTROSCOPY OF ADENINE ADSORBED ON MARTIAN METEORITE AS A TEST FOR A SEARCH OF EXTRATERRESTRIAL LIFE TRACES.

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**Introduction:** Surface Enhanced Raman Scattering (SERS) is a powerful technique for the chemical and structural analysis of minerals and organic molecules. This technique provides an huge enhancement of the Raman signal by means of the interaction with silver, gold or copper nanoparticles [1]. In recent years this technique has gained a increased attention especially for the study of trace biological molecules, owing to its high sensitivity, without sample preparation or manipulation. The possibility to employ "in situ" this technique, as well as the feasibility of instrumental miniaturization, makes it potentially suitable in the extraterrestrial exploration [2, 3].

Since microbial life, if extinct or extant on Mars, would give rise to the formation of biomolecules that could be adsorbed on rocks and sediments, the SERS investigation of nucleic acids is important to understand if and how primitive life originated in extraterrestrial environments. Two main limitations usually impair the employment of the conventional Raman technique for this purpose, the low sensivity and the occurrence of fluorescence, which could interfere with the observation of vibrational bands. The SERS spectroscopy allows overcoming these issues, by detecting absorbed molecules up to subpicogram level [3].

Before undertaking a Raman investigation directly on Mars surface, we preliminarly want to test the SERS response of biological molecules on Martian meteorites present in the collection of the Museo di Scienze Planetarie in Prato (Italy). Here we report the results of a SERS investigation on DAG 670 meteorite (Martian shergottite) [4] where adenine, a nucleobase detected in several meteorites [5-7], has been deposited.

**Experimental:** A thick slide of the DAG 670 meteorite was polished with diamond slurry down to 0.25µm, ultrasonically cleaned with water, rinsed with bidistilled water and air dried. Then, a drop of dilute (~ $10^{-2}$ $mol.dm^{-3}$) water solution of adenine was deposited on the surface. Once the solvent was evaporated a drop of silver colloidal nanoparticles were add. The main components of this meteorite are olivine ($Fo_{58-80}$), pigeonite, pyroxene ($En_{56-66}Wo_{9-13}$) with subordinate opaque phases (chromite, titanian chromite, ilmenite) (figure 1). Different grains of the three most significant mineralogical phases were randomly chosen on the sample surface and there, Raman spectra were recorded by using an excitation laser line in the red light region (632.8 nm). The experiments were performed before and after addition of silver nanoparticles. Since the substrate crystallographic orientation affects the spectra as well as the occurrence of fluorescence, we repeated the experiments on the same crystalline regions.

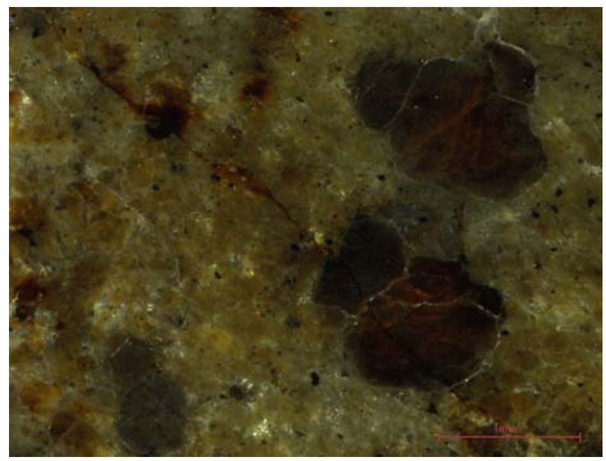

Fig 1. Optical image of a portion of DAG 670 (Martian shergottite) thick section. The meteorite is composed of mm-size brown olivine, pyroxene and opaque phases.

**Results:** Without depositing Ag colloidal particles, no Raman band attributable to adenine can be observed, but only those corresponding to the different mineralogical components of the rock (Fig 2 and 3).

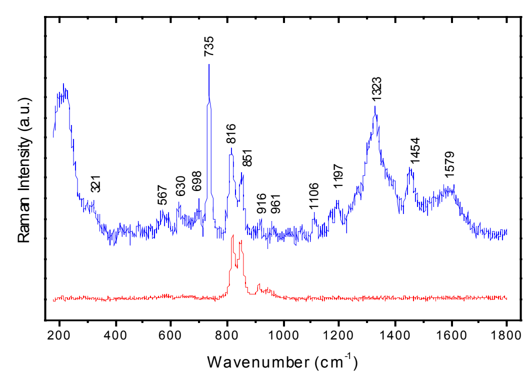


Fig 2. Raman spectra of adenine adsorbed on DAG 670 olivine before (red line) and after (blu line) the addition of silver nanoparticles.

After the addition of Ag nanoparticles the adenine marker bands are, instead, observed in the sample regions corresponding to pyroxene and olivine mineralogical phases. The adenine Raman modes resulted enhanced overtaking the signal coming from the substrate (Fig 2 and Fig 3).

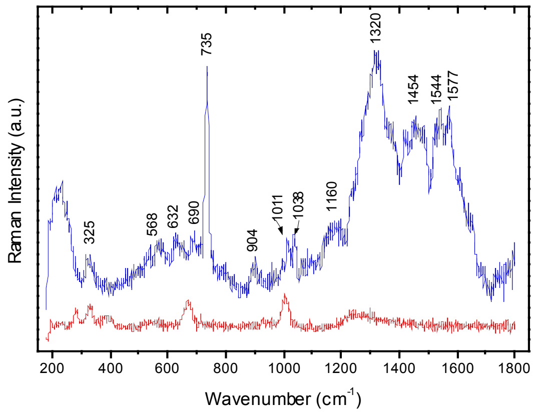


Fig 3. Raman spectra of adenine adsorbed on DAG 670 pyroxene before (red line) and after (blu line) the addition of silver nanoparticles.

Fluorescence bands were also observed; however, the adenine SERS bands, especially that at 735 $cm^{-1}$, were much stronger, allowing unambiguous assignment. A Different situation was observed on ilmenite where no appreciable adenine band was detected even after the addition of Ag nanoparticles (Fig 4).

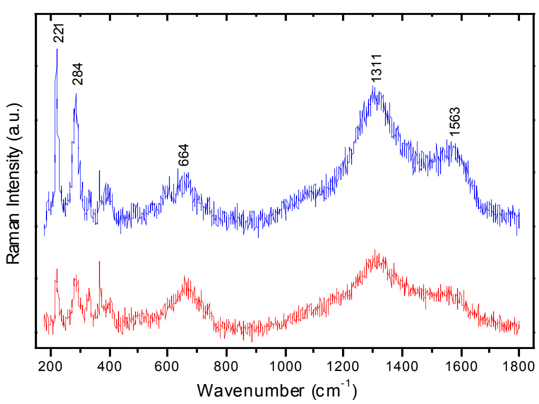


Fig 4. Raman spectra of adenine from DAG 670 ilmenite before (red line) and after (blu line) the addition of silver nanoparticles.

**Conclusion and Perspectives:** Experimental evidence of the capability of SERS technique to detect traces of nucleobases on rock surfaces was obtained. For the first time a Martian meteorite (shergottite) was used as substrate for the SERS investigation, which has been applied to different mineralogical phases considered to be representative of Martian basalts. The Raman bands of adenine were enhanced by SERS effect allowing a clear identification of this nucleobase as small trace. Considering the drop volume, the adenine concentration, the wetted sample and laser spot areas, the adenine amount responsible for the SERS spectrum is about $10^{-12} \div 10^{-13}$ g. By using, the red-light laser excitation (632.8 nm) limited fluorescence phenomena occur which, however, do not impair the observation of adenine.

We are currently improving the procedure employed in the spectroscopic investigation, which will be extended to biomolecules detected in other meteorites.

**Acknowledgements:** The authors would like to thank Regione Toscana for financial support of the project LTSP through the fund POR FSE 2007-2013 (Obiettivo 2, Asse IV).

**References:** [1] K. Kneipp et al. (Eds) (2006), Surface-Enhanced Raman Scattering: Physics and Applications; [2] W. Kiefer, J. Raman Spectrosc. (2004), 35, 427; [3] M. Muniz-Miranda et al., J. Raman Spectrosc. (2010) 41, 12–15; [4] L. Folco et al., Met. Plan. Sci. (2000) 35, 827-839; [5] Z. Martins et al., Earth Plan. Sci. Lett. (2008) 270, 130-136; [6] R. Hayatsu et al., Geochim. Cosmochim. Acta (1975) 39, 471–488; [7] P.G. Stoks, A. W. Schwartz, Nature (1979) 282, 709–710.