

**SERS INVESTIGATION OF NUCLEOBASES DEPOSITED ON EVAPORITE MINERALS: A TEST CASE FOR ANALOGUE MARS REGOLITH.** S.Caporali<sup>1,2</sup>, V.Moggi-Cecchi<sup>1</sup>, M. Pagliai<sup>2</sup>, G.Pratesi<sup>3</sup>, V. Schettino<sup>2,4</sup>, <sup>1</sup>Museo di Scienze Planetarie, Provincia di Prato, Via Galcianese, 20/h, I-59100 Prato, Italy, <sup>2</sup>Dipartimento Chimica, Università di Firenze, Via della Lastruccia, 3, I-50019, Sesto Fiorentino, Italy, e-mail: [stefano.caporali@unifi.it](mailto:stefano.caporali@unifi.it), <sup>3</sup>Dipartimento di Scienze della Terra, Università di Firenze, Via La Pira, 4, I-50121, Florence, Italy, <sup>4</sup>European Laboratory for Non-Linear Spectroscopy (LENS) Università di Firenze, Via Carrara 1, I-50019, Sesto Fiorentino, Italy.

**Introduction:** Traditionally, Micro-Raman spectroscopy is one of the primary analytical techniques for the detection of minerals and organic molecules in the laboratory. However, in owe of its versatility and capability to interrogate samples without preliminary purification or concentration treatments, it is one of the frontrunners for the next generation of in situ instrument designed to explore Solar System bodies. In particular the Raman capability to unambiguously detect organic molecules and biomarkers might result of great importance to understand if and how primitive life generates in extraterrestrial environments (e.g. Mars). The technique's analytical sensitivity towards organic molecules can be further enhanced by means of the interaction with coin metals nanoparticles [1]. This approach, named Surface Enhanced Raman Scattering (SERS) has proved to be able to detect traces amount of nucleobases adsorbed on Terrestrial [2] or Martian [3, 4] substrates. Even if these studies have shown the suitability of SERS to detect tiny amounts of biomarkers in magmatic rocks, other substrates such as evaporites should result more prone to host biomolecules. According to orbital and rover observations [5, 6] as well as the presence of tiny amounts of evaporitic minerals in nakhlites (Martian meteorites) [7], Martian evaporites are considered to be constituted by carbonates, sulphates and clay minerals. In the present study we focused on the identification of nucleobases on Martian analogue material in order to test the SERS response on such kind of mineral substrates.

**Results and Discussion:** Two different nucleobases (adenine and hypoxanthine, Figure 1) were deposited on crushed samples made of carbonates (calcite, dolomite, magnesite and siderite) and sulfates (anhydrite and gypsum).

Then the Raman spectra were collected under air at room temperature on every single mineral phase. Without depositing Ag nanoparticles (Ag-nps) only the bands attributable to the substrate were observed (Figure 2).

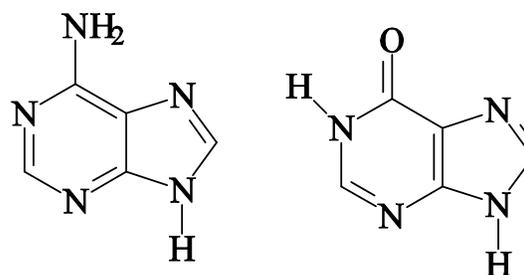


Figure 1: Structure of adenine (left) and hypoxanthine (right).

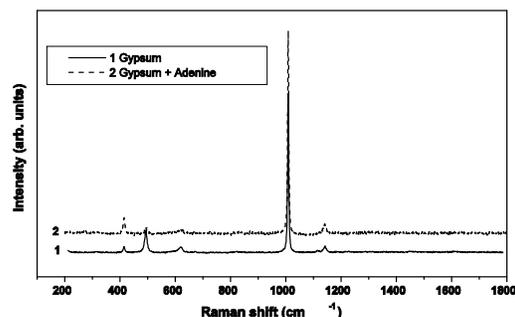


Figure 2: Raman spectra collected on a single grain of gypsum after (curve 1) and before (curve 2) the addition of the adenine dilute solution. Both spectra are dominated by the vibration bands attributable to gypsum. No adenine bands are detectable.

The addition of Ag-nps dramatically changes the appearance of these spectra. Alongside the broad band at 230-250  $\text{cm}^{-1}$  related with the Ag-nps and assigned to the Ag-Cl and Ag-N stretching modes, the Raman modes of adenine and hypoxanthine become clearly detectable (Figure 3). Apart from a large series of unresolved peaks in the spectral region between 1200 and 1700  $\text{cm}^{-1}$ , attributable to overlapping vibrational modes present in both the molecules, intense and characteristic bands in the range between 700 and 750  $\text{cm}^{-1}$  are observed. The presence of the 734  $\text{cm}^{-1}$  peak is univocally assigned to the adenine breathing mode [8] while the two peaks at 726 and 743  $\text{cm}^{-1}$  are

assigned to the hypoxanthine breathing mode in neutral and anionic forms, respectively [9].

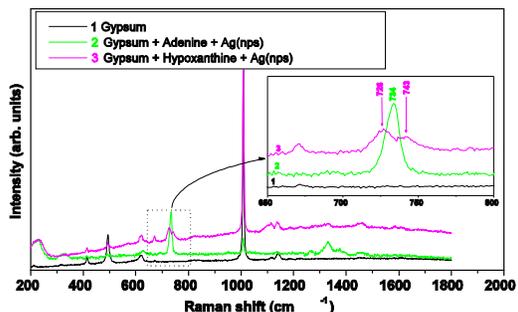


Figure 3: Raman spectra collected on a single grain of gypsum before (black line) and after the addition of adenine (green line) and hypoxanthine (magenta line) and Ag-nps. The inset shows a detail of the spectra in the 650-800  $\text{cm}^{-1}$  range.

The approximate quantity of sample responsible for SERS signal can be estimated assuming a uniform distribution of the nucleobases on a wetted surface area of  $\sim 20 \text{ mm}^2$  and a laser spot of  $\sim 3 \mu\text{m}^2$ . In such conditions the amount of sample involved in the SERS spectra is at level of  $10^{-12}$ - $10^{-13}$  g. Furthermore, among the tested substrates very slightly frequency shifts were observed [10], allowing to consider the peak at 734 and the two peaks at 726 and 743  $\text{cm}^{-1}$  as reliable markers for the identification of adenine and hypoxanthine, respectively.

**Conclusions and Perspectives:** Experimental evidence of the capability of SERS technique to detect traces of adenine and hypoxanthine deposited as dilute solution on evaporite minerals was provided. The Raman bands of these nucleobases were enhanced by SERS effect allowing their identification as small traces (about  $10^{-12}$ - $10^{-13}$  g). The results here displayed suggest the adoption of SERS as analytical procedures for *in situ* investigation on Mars. This only requires for Raman spectrometer adopted for the ESA ExoMars mission the most appropriated wavelength laser source and an automatic Ag hydrosol sprayer.

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**References:** [1] K. Kneipp et al. (Eds) 2006. *Surface-Enhanced Raman Scattering: Physics and Applications*; [2] M. Muniz-Miranda et al. 2010. *Journal Raman Spectroscopy* 41:12-15; [3] El Amri C. et al. 2004. *Journal Raman Spectroscopy* 35:170-177; [4] S. Caporali et al. 2011. Abstract #1401. 42<sup>th</sup> Lunar and Planetary Science Conference; [5] Bibring J-P. et al. 2005. *Science* 307:1576-1581; [6] Chevrier V. and Math P.E. 2007. *Planetary and Space Science*, 55:289-314; [7] Bridges J.C. and Grady M.M. 2000. *Earth and Planetary Science Letters* 176:267-279; [8] Giese B. and McNaughton D. 2002. *Journal Physical Chemistry B* 106:101-112; [9] Chowdhury J. et al. 2000. *Journal Raman Spectroscopy* 31:427-431; [10] Caporali S. et al 2011, *Spectroscopy Letters* 44:580-584.