ADENINE ADSORBED ON A MARTIAN METEORITE AS A TEST CASE FOR SERS INVESTIGATION OF EXTRATERRESTRIAL LIFE TRACES. S. Caporali[1,2], V. Moggi-Cecchi[1], M. Muniz-Miranda[2], M. Pagliai[2], G. Pratesi[3], V. Schettino[2], [1] Museo di Scienze Planetarie, Via Galcianese 20/h, I-59100 Prato, Italy, [2] Dipartimento di Chimica, Università degli Studi di Firenze, Via della Lastruccia 3, 50019, Sesto Fiorentino, Italy, e-mail stefano.caporali@unifi.it, [3] Dipartimento di Scienze della Terra, Università degli studi di Firenze, Via G. La Pira 4, I-50123 Firenze, Italy, e-mail g.pratesi@unifi.it

Introduction: Surface Enhanced Raman Scattering (SERS) is a powerful technique for the chemical and structural analysis of minerals and organic molecules. This technique provides a huge enhancement of the Raman signal by means of the interaction with silver, gold or copper nanoparticles [1]. In recent years, owing to its high sensitivity, this technique has gained an increased attention especially for the study of trace biological molecules.

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. Even if SERS spectroscopy allows overcoming these issues [2,3] its suitability to be used as "in situ" technique for direct investigation on Mars surface still remains to be assessed [4].

In this contribution we report the results of a SERS investigation on DAG 670 meteorite [5] (Martian shergottite) where adenine, a nucleobase detected in several meteorites [6-7], has been deposited.

Experimental: A thick slide of the 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.

Results: Aiming to find the optimal experimental conditions for the detection of adenine in a real Martian rock we carried out SERS investigation on three mineralogical phases constituting the main part of the meteorite (olivine, orthopyroxene and ilmenite) by means of three different excitation laser lines; two in the red light region (632.8 nm and 785 nm) and one in the green light region (514.5 nm). In such a way we collect an accurate owerview of the Raman signal as function of the substrate as well as the excitation laser wavelength. The results show adenine can be unambiguously identified by detecting the intense SERS band located at ~735 cm^{-1}, which frequence results practically unaffected by the nature of the substrate. However, silicate substrates (olivine and orthopyroxene) result more prone to give intense and sharp peaks respect to the oxides (ilmenite) and therefore they should be preferred for analytical purposes. On the other side, fluorescence phenomena were greately enhanced when short excitation wavelength were employed turning in a much lower analytical performace for the green light region excitation laser respect to the red ones.

Furthetmore, we extend these investigations also to salted silver nanoparticles. Adding salt (LiCl) to the Ag hydrosols results in the increase of the colloid zero potential. It turns in the enhanced solution stability (many months under Earth's gravitational attraction without marked aggregation) respect to the unsalted one. Experimental evidence show no appreciable differences between the two types of silver colloidal nanoparticles.

Conclusion and Perspectives: Experimental evidence of the capability of SERS technique to detect traces of adenine on Martian-type rock (Martian shergottite, DAG 670) were provided allowing a clear identification of this nucleobase as small trace (about $10^{-12} \div 10^{-13}$g). We also demonstrated the use of red-light laser excitation helps to limit the fluorescence phenomena, while the use of LiCl-stabilised silver nanoparticle does not infer in the thecnique analytical performance allowing the use of this more stable Ag hydrosol.

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