GARATÉA II MISSION: The Earth's Stratosphere as a Mars Analogue Environment for Potential Molecular Biosignatures' Studies and Space Missions Application

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Introduction

The search for **biosignatures** is still challenging in terms of the selection of good targets as well as their detection.

Raman spectroscopy has emerged as a powerful, non-destructive and noncontact analytical technique, that offers spatially resolved and high sensitivity detection and characterization of *in situ* organics and associated minerals.

It is a potential alternative to destructive methods, such as pyrolysis (used by Curiosity's instrument to detect organic compounds on Mars [1]), and will be part of both **ESA's ExoMars** in 2018 and **NASA's Mars 2020** missions. [2,3,4]

The selection and detection of potential biosignatures also depends on their resilience in the **extreme conditions** of extraterrestrial environments (mostly UV radiation of stars).

Earth's stratosphere - 12 to 50 km above sea level - can mimic the harsh conditions of the **surface of Mars** (low pressure and temperature combined with high radiation and dryness). Unlike Mars, however, the stratosphere is accessible and affordable to reach via **high-altitude balloons**, what makes it an interesting test-bed for astrobiology experiments, as well as validation for life-detection instrumentation and methodology.

A balloon gondola was designed and built by the Zenith group (University of São Paulo), named **Garatéa** ("searching for life"). Launched in December 19th 2016, it travelled through the stratosphere for about 1 hour, reaching a maximum altitude of 25.5 km ASL. The environmental collected data is shown in Table 1. An instrument malfunction prevented the acquisition of the UV flux measurements during our balloon flight. For comparison, data found in the literature is also shown.

Table 1. Physical conditions on Earth's stratosphere and Mars surface.

Parameter	Mars (surface)	Earth (12-25 km)
Pressure	6.3 mbar [a]	193 - 11 mbar [b] / 50 mbar [c]
Temperature	213 K [a]	253 - 279 K [b] / 203 - 233 K [d]
RH	~0 % [a]	1 - 2.6 % [b] / ~ 1 % [d]
Solar constant	589.0 W/m² [a]	1367 W/m² [a]
UV (A, B, C) (200-400 nm)	(38.39, 8.38, 3.18) = 50.6 W/m² [e]	(82.35, 4.16, 0.0055) = 86.6 W/m² [f]

a: [5], **b:** Min. and max. measured values between 12 and 25 km (flight) [Garatéa] **c:** Value measured at 20 km (flight) [6], **d:** Min. and max. measured values between 12 and 25 km (flight) [7], **e:** Estimated as 43% of Earth's solar constant, calculated from model at 20 km [8], **f:** calculated from model at 20 km [9].

Materials and Methods

Three sets of 14 samples in duplicate were prepared:

E: flew in the balloon and was **"Exposed to radiation"**

N: flew in the balloon, but was **"Not exposed to radiation"**

C: maintained on the lab to be a **"ground Control"**

Synthetic diamond powder (standard for quantification, robust and inert) [10] and 3 µL of water (to facilitate any reaction) were added to all biomolecules, listed on Table 2. Only DL-cysteine was sent both pure and mixed with 5 inorganic substrates, relevant to the Martian surface.

The analysis was made using a Renishaw inVia micro **Raman spectrometer** with a 785 nm excitation laser.

Table 2. Samples sent in Garatéa II mission.

Class/Type	Sample	Class/Type	Sample
Fullerene	Fullerene	Amino acid	DL-cysteine
Biological pigment	β-carotene	Amino acid dimer	L-cystine
Nucleic base	Guanine	Clay	Kaolinite (KG_{a-2})
Bacterium	*Deinococcus Radiodurans*	Martian Soil Simulant	JSC-Mars 1A
Porphyrin	Hemin	Iron Mineral	Goethite
Nucleoside triphosphate	Adenosine triphosphate	Clay	Montmorillonite (Sy_{n-1})
Carboxylic acid	Fumaric acid	Salt	$MgSO_4.7H_2O$

Results

Figure 3 shows the normalized spectra of (a) **DL-cysteine,** (b) **DL-cysteine + Kaolinite** and (c) **β-carotene**, with peak assignments [11, 12] after being (or not) submitted to the stratospheric conditions. It is possible to observe increases or decreases in the peaks intensities, which can be a sign of bond formation or breaking. The quantitative analysis (area and intensity) with respect to the diamond peak (1333 cm^{-1}) can give more detailed and reliable results (**Figure 4**).

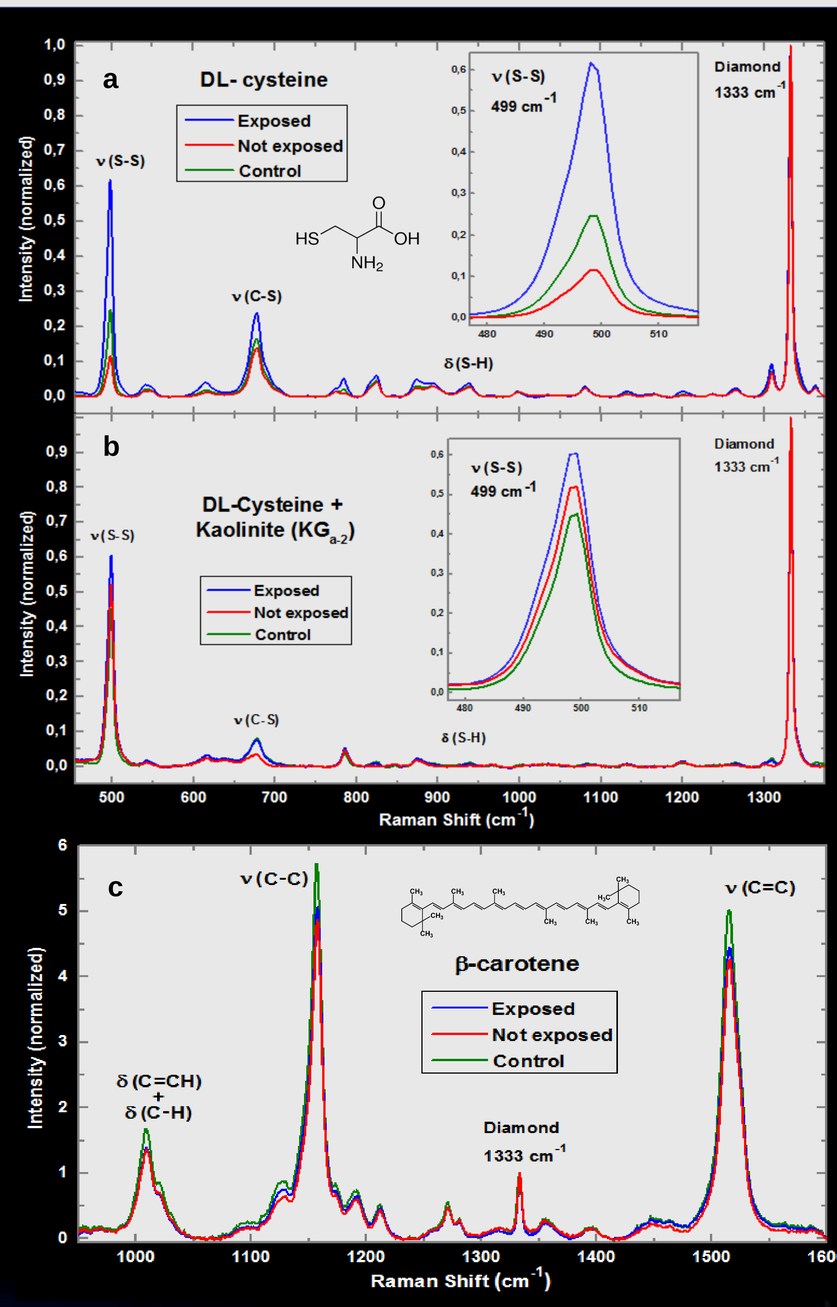

Figure 3. Raman spectra of (a) DL-cysteine (b) DL-cysteine + Kaolinite and (c) β-carotene (average of 20 spots in the samples).

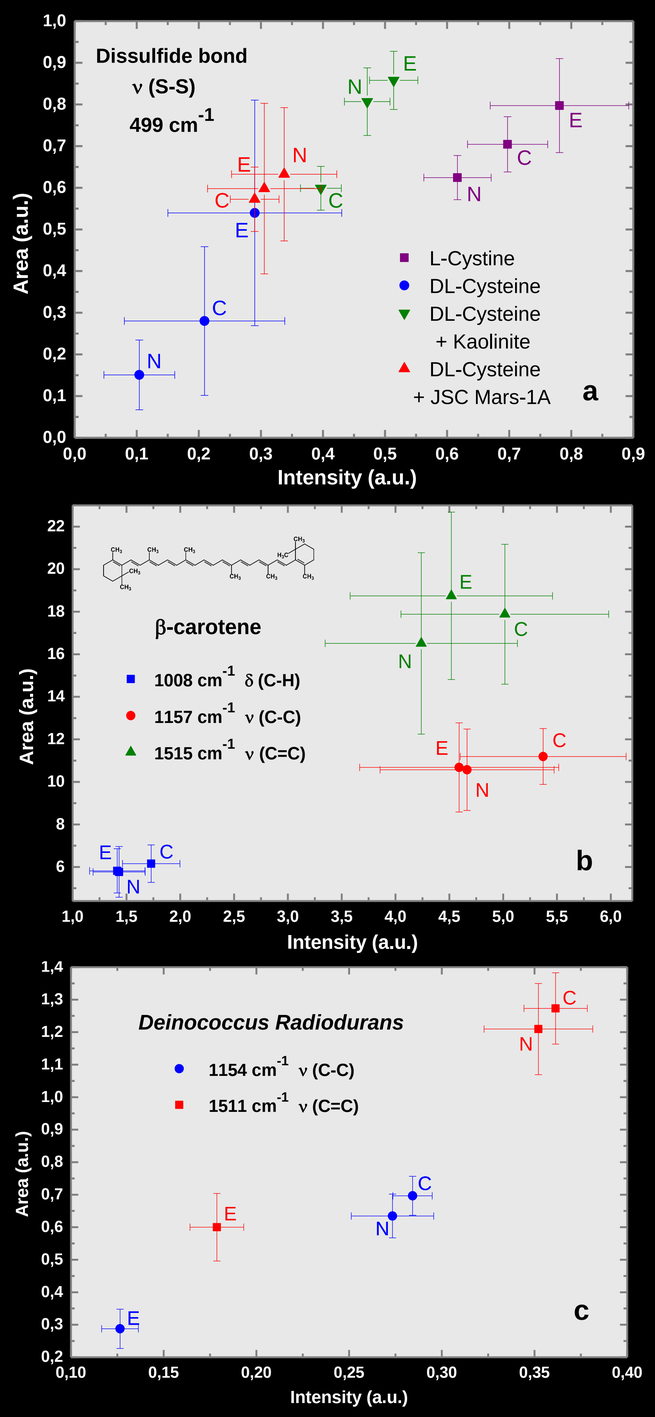

Figure 4. Area and Intensity maps of (a) Dissulfide bond (S-S) in different samples, (b) β-carotene peaks and (c) *Deinococcus Radiodurans*' carotenoids peaks

Discussion and Conclusions

Results show that **Raman spectroscopy** is in fact a powerful technique for biomolecules' detection and characterization, even if mixed with inorganic substrates. The large error bars on Fig. 4 may indicate that either the number of spectra acquired was too low for a good statistic analysis, or the samples had an intrinsic variability. Besides that, it is possible to see changes in the peaks areas and intensities. And **high-altitude balloons** have proven to be a reliable research platform to probe the **stratospheric** environment as well as to validate space mission's experiments and instrumentation. Laboratory simulations and new flights with more complex setups are being planned to support a future mission in a **CubeSat**, already in preparation by the group, with planned launch to the Moon's orbit in 2020 – the **Garatéa-L** mission.

Credits: ZENITH/GARATÉA

Figure 1. Garatéa II prepared to the flight.

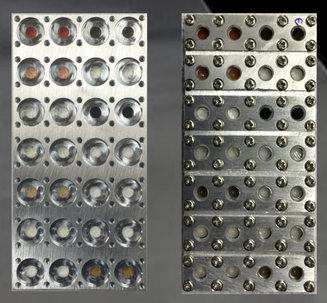

Figure 2. Aluminum sample holder with samples (Left) open and (Right) closed with Ultralene® film, o-rings, aluminum lids and screws.

Background. Garatéa-II in the stratosphere exposing biomolecules and microorganisms.

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