RAMAN ANALYSIS OF PIGMENTS FROM MESSINIAN GYPSUM ENDOLITHS

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Abstract

Endolithic microorganisms are known model organisms in astrobiological studies. Their habitats within the mineral matrix could represent hypothetical refugia of Martian biota given that Martian surface is very hostile to known life [1]. On Earth, semi-translucent or translucent minerals such as gypsum seem ideal habitats for endoliths since they can buffer outside conditions (e.g. fluctuation in temperatures, increased UV irradiation and desiccation) but still allow light penetration for photosynthesis. Besides that, various protective pigments are synthesized by endolithic microorganisms. Carotenoids, porphyrins, scytonemin are examples of important biomarkers for astrobiology [2]. In the upcoming Martian missions – ExoMars and Mars 2020, miniaturized Raman spectrometers will aim to find potential biomarkers of extinct or extant life [3].

In this work we show advantages and limits of Raman spectrometric investigations for detecting and discriminating pigments in endolithic colonization. A miniature portable Raman spectrometer was used for analysis of endolithic colonies directly at several outcrops of Messinian gypsum in south-western Sicily. Here the portable system mostly allowed screening of carotenoids *in situ*. Individual coloured layers were screened separately on outcrops. Raman spectra show the presence of carotenoids by obtaining strong bands corresponding to the stretching vibrations of the polyene chain of carotenoids. However, the exact identification of carotenoids in the living cells by portable Raman spectrometer is limited, as various microorganisms are present in colonies and each cell may contain different pigments. This is also connected to the fact that Raman spectra are collected from portions of samples of about 10-100 μm. Still, the evaluation of the performance of miniature Raman systems working *in situ* on gypsum series inhabited by cyanobacteria, algae, bacteria is significant for the forthcoming Martian missions.

Furthermore, the laboratory investigation using a dispersive Raman microspectrometer permitted to better understand distribution of carotenoids at micrometric level as well as to indicate the presence of other protective pigments. In several samples signals of scytonemin, chlorophyll or phycobiliproteins were recorded.

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