

# Models of chemical biosignatures – a vibrational spectroscopic study

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## Abstract

Investigating possible biosignatures is of central interest in the search for the oldest traces of terrestrial life. Possible biosignatures are: (i) physical structures, such as fossilized single-celled or colony-forming microorganisms; (ii) biomolecules and their altered residues (chemical biosignatures); (iii) altered element, isotope and mineral compositions in former microbial habitats and related effects caused by metabolic activity [1]. New insights in this field of research are also important in the search for life on other planets and moons, especially Mars. However, abiotically formed organic compounds are widely distributed in the universe. Therefore, in future Mars missions, it will be essential to know whether organic molecules are actually of biological origin. Here, we describe the syntheses and spectroscopic (Raman and infrared) properties of artificial chemical biosignatures that might help answering this question.

## 1. Introduction

Environmental similarities in the early histories of Earth (Hadean/early Archean eon) and Mars (Noachian eon) gave rise to the idea that life might have emerged on both planets during this time [2]. Micro-organisms might once have inhabited or might still inhabit deeper soil layers of the Martian surface [3]. In both cases, biosignatures will be embedded in mineral matrices and should be detectable by analytical instruments on future Mars missions. Raman spectroscopy is a powerful tool for analyzing combinations of organic components (e.g., carbonaceous materials [4]) and minerals.

### 1.1 Carbonaceous materials

The chemical structure of carbonaceous materials gives rise to a characteristic Raman spectrum, which is composed of two regions (1st and 2nd order re-

gion). Two bands, called G and D1, dominate the 1st order region. The G band is caused by the graphite structure. Its intensity increases with increasing crystallinity. The D1 band mirrors structural defects due to heteroatoms (e.g., N and O) or hydrocarbons and is absent in perfectly crystallized graphite. The D2 band appears as a shoulder of the G band. The S1 band is the dominant signal in the 2nd order region. The presence of carbonaceous material is no definite evidence of a biological origin as it can also be formed through abiotic processes [5, 6].

### 1.2 Mineral matrices

Chemical biosignatures will very probably not exist as clusters of pure material but in more or less intimate mixtures with mineral matrices. Possible matrices include basaltic rock, volcanic ash, phyllosilicates and evaporites (salts). Such potential matrices are not only found on Earth but also on Mars. For example, many different phyllosilicates have already been detected on the Martian surface [7, 8].

## 2. Materials and Methods

We chose the widespread biomolecules heme (in the form of hemin) and lecithin as starting materials for the synthesis of chemical biosignatures. They were heated at different temperatures of 200, 500, and 900 °C for 48 h to simulate thermal alteration as one possible alteration process. A whole organism, the cyanobacterium *Spirulina laxissima*, was treated in the same way. In addition, the biomolecules and *S. laxissima* were separately mixed with the phyllosilicate kaolinite prior to the thermal treatment. In order to simulate the oxygen-free conditions on early Earth and Mars, a special thermolysis apparatus was used which ensured the complete exclusion of oxygen during the thermal treatment [9]. The thermally treated samples were analyzed by Raman and Fourier transform infrared spectroscopy.

### 3. Results

The two biomolecules and the dried *S. laxissima* cells were essentially chemically stable up to 200 °C. Only some slight changes occurred in the 400–1500 cm<sup>−1</sup> region of the infrared spectra. Heating at 500 °C, however, resulted in the total loss of any characteristic infrared signals such as the C–H stretching bands of the CH<sub>3</sub> and CH<sub>2</sub> groups. For the two biomolecules, this decomposition was confirmed by the Raman spectra that showed the typical signals of carbonaceous materials (see above). After thermal treatment at 900 °C, only one biomolecule, namely hemin, left a measurable residue. In the Raman spectrum of this residue, the characteristic features of carbonaceous material appeared even more clearly (Fig. 1). Through mixing of the biomolecules and the microorganism with the mineral matrix kaolinite, the analysis of the thermal residues became more complicated. Especially in the infrared measurements, signals of the mineral matrix superimposed parts of the biomolecule spectra, thereby prohibiting the proper evaluation of changes that might have resulted from the thermal treatment. In contrast, an adequate analysis of the spectral changes was still possible by Raman spectroscopy, despite the sometimes interfering fluorescence.

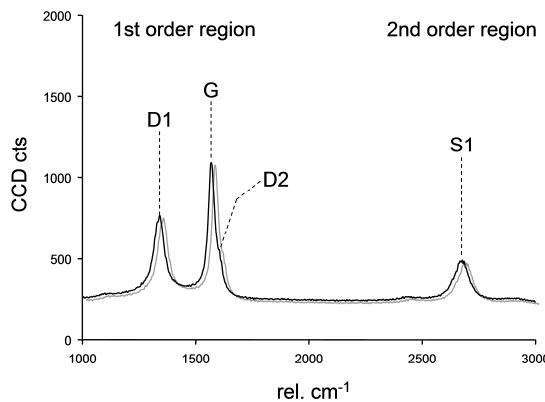


Figure 1: Raman spectrum of carbonaceous material formed by thermal treatment of pure hemin at 900 °C.

### 6. Summary and Conclusions

Thermal treatment of the biomolecules hemin and lecithin and the microorganism *S. laxissima* at temperatures well above 200 °C resulted in total decomposition. In the case of the biomolecules, the formation of carbonaceous material was unequivocally ob-

served. Raman spectroscopy proved to be a suitable method to analyze the residues. Carbonaceous materials can form from non-biological sources. Thus, it is necessary to have criteria that distinguish between carbonaceous materials of biotic and abiotic origin. Future experiments with other biomolecules and mineral matrices as well as modified experimental parameters might help to further develop such criteria.

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