

Ancient life on Mars and infrared spectroscopy of Earth analogues

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One of the main aims of the next Mars space missions will be to characterize biochemically the surface and underground of the planet in the search for elementary forms of life. Laboratory analyses devoted to the study of techniques able to recognize the biological origin of samples, carried out on Earth analogues of Martian ground, are fundamental support for the planning of suitable instrumentation and the subsequent analyses of data.

Here we present the results of infrared transmission spectroscopic studies on old biological carbonates with different degrees of degradation, including carbonates linked to primitive terrestrial living organisms (fossil stromatolites), performed to evidence spectroscopic peculiarities and their likely dependence on the age of formation.

On Earth, the main polymorphs of calcium carbonate (CaCO_3), aragonite and calcite, are produced by abiotic as well as biological activity. By means of Differential Thermal Analysis (DTA) (Mackenzie, 1970), it is possible to study the endothermic transformation from the metastable form of aragonite to the stable form of calcite and the transformation, at higher temperatures, of calcite into solid calcium oxide (CaO) and gaseous carbon dioxide (CO_2) (Stalport *et al.*, 2005; 2007). Using infrared (IR) spectroscopy, it is possible to distinguish various polymorphs of calcium carbonate and understand how much the decomposition process, following the thermal processing, has gone on. According to this experimental result, we performed transmission spectroscopy in the Mid Infrared range (MIR; 2000-400 cm^{-1} or 5-25 μm) in order to study physical properties and examine the behaviour after heating of biotic and abiotic samples starting from tested temperatures in DTA measurements. The aim was to highlight discriminating factors useful to differentiate between abiotic minerals and biominerals.

In D'Elia *et al.* (2006) and Orofino *et al.* (2007) we analysed the reaction to heat treatments of biotic and abiotic fresh and fossil samples mainly composed of CaCO_3 . We chose recent shells and fresh stromatolites (max 10 years old), relatively young fossils of calcite and aragonite structure dating from Lower/Middle Pleistocene (0.8-1.8 Myr) and Oligocene (23-34 Myr), and an Ar-

chaean sample of fossil stromatolites 3.5 Gyr old.

In the present work we report on our studies about fossils of other geologic epochs, that maintained their calcite structure (*Haliotis lamellosa* gastropoda dating from Oligocene and fossil stromatolites dating from Meso-proterozoic) in order to study the spectral reaction to heat processing of differently preserved biological structures, highlighting the appearance and evolution of the CaO band after heating. It is important to underline that the Meso-proterozoic stromatolites (1.2 Gyr old) are not completely mineralized and are still calcite so that it is possible to study their decomposition from carbonate into CaO.

In Table 1 we report the name of all the samples analysed in the present work and their estimated geological ages.

As described in our previous works (D'Elia *et al.*, 2006; Orofino *et al.*, 2007), every mineral and biomineral has been spectroscopically analysed before (unprocessed samples) and after (processed samples) heat processing at 485 °C. For details on the experimental procedure we refer the reader to Orofino *et al.* (2007).

Analysing the spectroscopic results, it is evident that the thermal processing induces different physical changes depending on the nature and the origin of the samples. As a matter of fact, the process of transformation from CaCO_3 into CaO and CO_2 is faster for "recent" biotic samples compared to the abiotic minerals so that the appearance of more or less pronounced structures in the spectra, due to the CaO band at 330 cm^{-1} (30 μm), can be considered a discriminating factor. The investigation of older fossils revealed that the fossilization process lead to an almost complete alteration of the intimate structure to a level that they spectroscopically behave like mineral calcite.

In order to study the formation of the CaO characteristic band, we focused on the spectral range 500 ÷ 650 cm^{-1} and introduced an index D, defined as the ratio between the spectral slope shown by the processed samples and that relative to the unprocessed ones. We observed that as D (always ≤ 1) increases, the spectral slope of the processed sample becomes more similar to that of unprocessed one, meaning that the thermal treatment is less affective in the transformation of CaCO_3 into CaO.

Sample	Name	Geologic period/epoch
1	<i>Tellina exigua</i>	Current (max 10 years)
2	<i>Cardites antiquata</i>	Current (max 10 years)
3	Fresh stromatolites	Current (max 10 years)
4	<i>Pecten sp.</i>	Middle Pleistocene, 0.8-0.1 Myr
5	<i>Ostrea sp.</i>	Lower Pleistocene, 1.8-0.8 Myr
6	<i>Myriapora truncata</i>	Lower Pleistocene, 1.8-0.8 Myr
7	<i>Haliotis lamellosa</i>	Oligocene, 34-23 Myr
8	Fossil stromatolites	Meso-proterozoic, 1.6-1.0 Gyr
9	Fossil stromatolites	Archean 3.8-2.5 Gyr
10	Calcite	—

Table 1
Labels, names and dating of the samples analysed in this work.

Index D can be seen as an index of fossil degradation, in the sense that $D \simeq 1$ implies the impossibility of discriminating between biotic and abiotic carbonate samples (for details see Orofino *et al.*, 2009). This means that the thermal processing do not produce transformation of the calcium carbonate into CaO or, at the most, it produces only slight modifications.

Fig. 1 reports the values of D for each sample, with the statistical dispersion, as a function of age in a logarithmic scale.

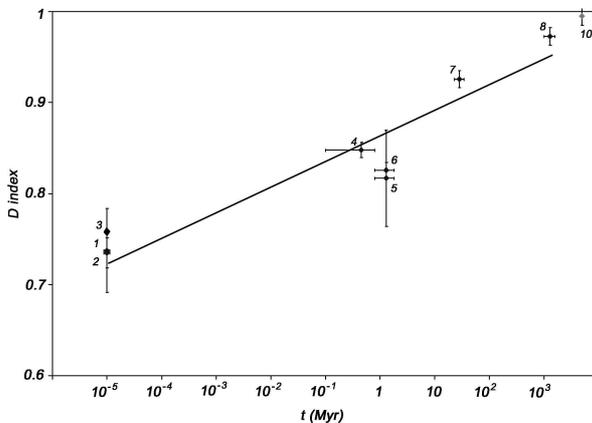


Figure 1. Slope variation index D. The labels correspond to the sample numbers in Table 1. The last point outside the chronological range refers to calcite mineral. The age of the samples have been taken according to the International Commission on Stratigraphy (Gradstein *et al.*, 2004).

As it can be seen, there exist the possibility of discriminating biotic from abiotic samples, up to about 1 Myr.

This could mean that the conclusions drawn by Orofino *et al.* (2007) on the efficacy of IR spectroscopy in discriminating between biotic and abiotic minerals could not be valid for samples

older than 1 Myr. However, while in the terrestrial environment the circulation of water in the ground has chemically altered the nature of biotic materials, the absence of such conditions on Mars for most of its history may have preserved some biotic signatures. In other words, due to the very different evolution of the environmental conditions on Mars and Earth, it is not unreasonable to think that the ancient Martian fossils, if they exist, may have experienced a degradation process slower than on Earth, in the sense that they could have attained a degradation level comparable to that of much younger terrestrial fossil.

We are now taking into consideration to analyse the spectral behaviour of more fossils of different age and origin in order to improve our studies and statistics.

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