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# The search for ancient life on Mars and the IR spectroscopy of Earth analogues

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**Abstract.** 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. We also report preliminary measurements using reflectance spectroscopy, a technique more likely to be performed directly *in situ* on the surface of Mars.

**Key words.** Exobiology – Mars – spectroscopy

## 1. Introduction

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 $\mu$m) 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

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

| Sample | Name | Geologic period/epoch |
|---|---|---|
| 1 | *Tellina exigua* | Current (max 10 years) |
| 2 | *Cardites antiquata* | Current (max 10 years) |
| 3 | Fresh stromatolites | Current (max 10 years) |
| 4 | *Pecten sp.* | Middle Pleistocene, 0.8-0.1 Myr |
| 5 | *Ostrea sp.* | Lower Pleistocene, 1.8-0.8 Myr |
| 6 | *Myriapora truncata* | Lower Pleistocene, 1.8-0.8 Myr |
| 7 | *Haliotis lamellosa* | 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 | — |

Oligocene (23-34 Myr), and an Archaean sample of fossil stromatolites 3.5 Gyr old.

Stromatolites are laminated structures built by the activity of cyanobacteria. The layers are produced as calcium carbonate precipitated over the growing mat of bacterial filaments. Stromatolites are key fossils for understanding the evolution of life (Walter et al., 1980). The high level of interest in the study of recent and fossil stromatolites also comes from the search for life on Mars. Mars and Earth probably shared similar early histories (McKay and Stoker, 1989). Undisputed evidence of life has yet to be discovered on the Red Planet but there is plenty of evidence that past environments may have been suitable for stromatolite growth. These fossils therefore provide important analogues for examining potential Martian fossils. Therefore, we spectroscopically studied fresh and Archaean stromatolites (D'Elia et al., 2006), and afterwards a specimen 1.2 Gyr old dating from Meso-Proterozoic period.

It is worthwhile to recall here that in the case of very ancient fossils, the fossilization could have completely mineralized the sample, as in the case of Archaean stromatolites transformed into quartz. 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 them. 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.

## 2. Measurements and results

For the reason discussed in the previous section, in the present work we extended our studies to 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

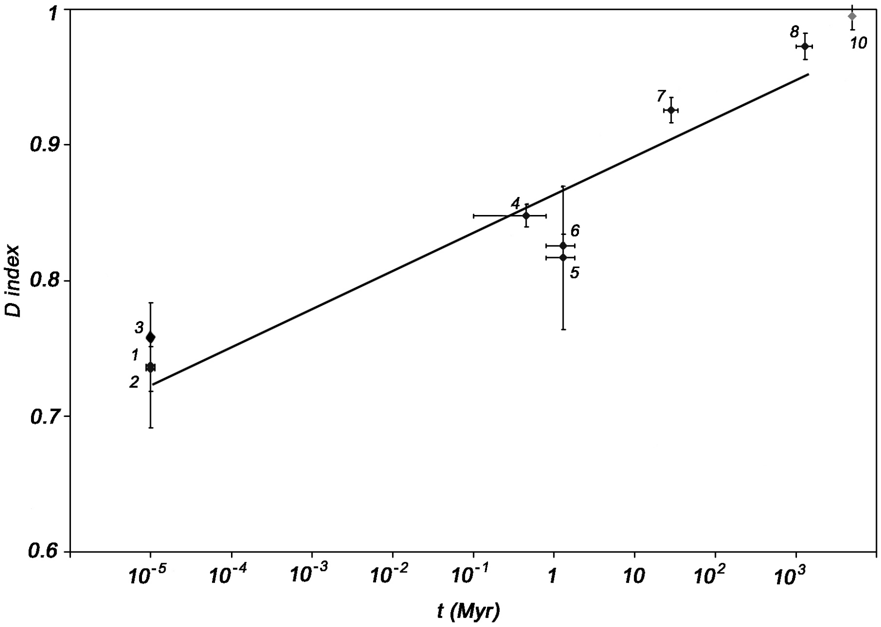


**Fig. 1.** Slope variation index D. The labels correspond to the sample numbers in Table 1. The last point outside the chronological range refers to calcite mineral. The age of the samples have been taken according to the International Commission on Stratigraphy (Gradstein et al., 2004).

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 $\mu$m), 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 $\leq 1$) 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.

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. 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. We remind that, analysing the 3.5 Gyr old fossils stromatolites (sample N. 9), the fossilization process completely changed the aragonite structure into quartz; traces of calcium magnesium carbonate, dolomite ($CaMg(CO_3)_2$), can be still de-

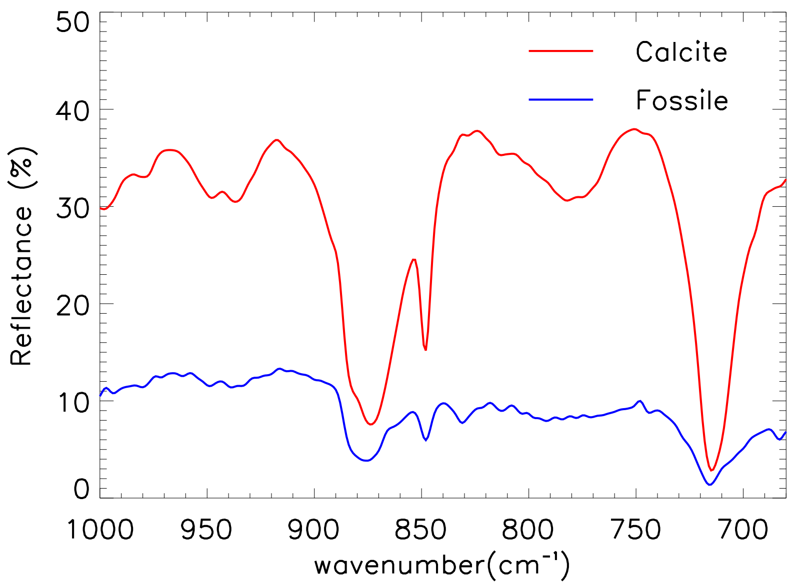


**Fig. 2.** Reflectance spectra of mineral calcite and a calcite fossil. The difference in the reflectance continuum is due to different grain size. The feature around 830 $cm^{-1}$ is the band under study.

tected with spectroscopy as evidenced also by the original composition (D'Elia et al., 2006). Unfortunately, the dolomite features are lost after the heat treatment so that it is impossible to reveal any kind of calcium oxide formation and therefore the study of its characteristic band. For this reason it is not present in Fig. 1

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.

Taking into account that this technique applies mainly to specimens brought back from Mars by sample-return space missions, we began to perform some preliminary measurements using, instead of transmission, reflectance spectroscopy which is more likely to be performed directly *in situ* on the surface of Mars.

Reflectance spectroscopy produces spectra very different from those of transmission. Fig. 2 shows an example of the IR reflectance spectrum of mineral calcite compared to that of a fossil of calcite composition in the wavenumber range between 1000 and 680 $cm^{-1}$ (wavelengths 10-14.7 $\mu$m).

As it can be seen, a feature at 830 $cm^{-1}$ is present in the spectrum of the fossil sample but not in the calcite mineral. We are trying now to understand if this difference can be a discriminating factor to distinguish biominerals from minerals as we did with the previous technique. The problem is not easy and more samples have to be considered in order to draw meaningful conclusions.

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