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A spectroscopic tool for the detection of biocarbonates

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Abstract. In previous laboratory work we have investigated the infrared spectral modifications induced by thermal processing on different terrestrial carbonates, in form of fresh shells and fossils of different ages, whose biotic origin is easily recognizable. The goal was to find a method able to distinguish between biotic and abiotic origin of the samples. In the present work we apply our analysis to problematic carbonate samples, in which there are no clear evidences of controlled or induced biomineralization. This analysis indicates a very likely biotic origin of the aragonite samples under study, in agreement with the conclusion previously reported by some of us who followed a completely different approach based on a complex set of sedimentary, petrographic, geochemical and biochemical analyses. We show that our method is actually reliable for discriminating between biotic and abiotic carbonates, and therefore it is a powerful tool for the search for life on Mars in the next generation of space missions to the planet.

Key words. Exobiology – Mars – spectroscopy

1. Introduction

Remote sensing and ground based observations performed during several missions strongly suggest that once Mars was warm and wet enough to allow the presence of abundant liquid water on the surface (Mars Pathfinder Rover team, 1997; Phillips et al., 2001; Craddock and Howard, 2002; Paige, 2005), due to a thicker atmosphere providing a strong greenhouse effect. More recently the study of the mineralogy of Mars has independently confirmed the above scenario of an ancient wet planet and suggested that several distinct habitable niches may have been present, providing a range of opportunities for the origin of life, including also places of impact-induced hydrothermal systems (Newsom, 1980; Gulick and Baker, 1989, 1990; Gulick, 1998; Marzo et al., 2010). This last hypothesis provides not only an interesting example of post-Noachian aqueous alteration on Mars, but also sites of extraordinary astrobiological potential.

Searching for traces of extinct or extant life is a major objective of Mars exploration, even though the detection of a biosignature is not a straightforward process. However, the probability of finding traces of biological ac-

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tivity would certainly be higher if the search is directed towards inorganic materials whose origin can be traced back to some form of life. This is the case of some terrestrial living organisms which are able to produce mineral matrices in the so called biomineralization process (Lowenstam, 1981; Mann, 1983, 2001). Nevertheless the problem of discriminating between biominerals and their abiotic counterparts is far from trivial. Fortunately, by means of thermal processing, it is possible to distinguish, using differential thermal analysis (Cabane et al., 2004; Stalport et al., 2005, 2007) or infrared (IR) spectroscopy (Orofino et al., 2007), abiotic calcium carbonate minerals ($CaCO_3$ i.e. aragonite or calcite) from the corresponding biominerals. In a series of recent papers we have developed and applied our method (D'Elia et al., 2007; Orofino et al., 2007, 2009, 2010) to different carbonate samples in form of fresh shells and fossils of different ages found in different places and easily recognizable as of biotic origin. In this work, applying our analysis to problematic carbonate samples, in which there are no clear evidences of controlled or induced biomineralization, we show that the method is really reliable, allowing to discriminate between biotic and abiotic carbonates.

2. Laboratory measurements and results

The carbonate samples used in our study come from the Calcare di Base (CB) formation, which crops out in the Rossano Basin (Northern Calabria, Italy) and formed in the Late Miocene (Messinian, ~ 6 Myr - see below). In the study area the CB succession consists of two massive fine-grained calcareous beds interlayered with decimetric laminated marls. In such geological settings the CB formation is massive, without any evidence of evaporitic minerals, and is preserved as aragonite.

The six bulk CB samples, labelled CB1-CB6, were collected near the village of Cropalati and selected according to their position in the stratigraphic succession (see Fig. 1) and to the features observed in the field. These

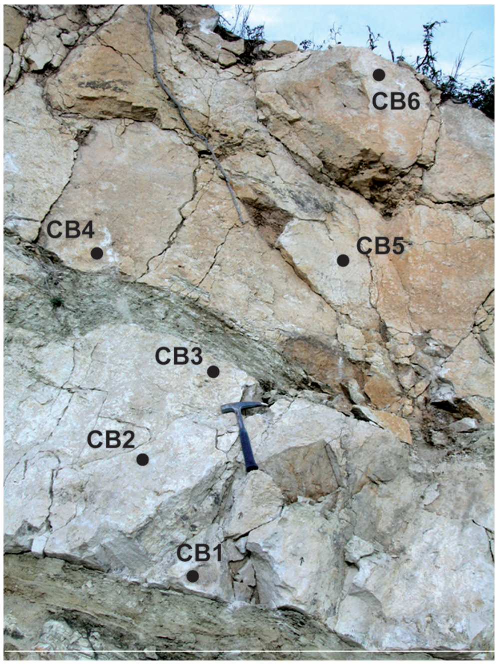

Fig. 1. Study section showing the position where the six samples of Calcare di Base have been collected.

samples were previously studied and characterized through molecular fossils and other organic markers (Guido et al., 2007).

The origin of these deposits (biotic versus abiotic) is not clear, due to the absence of fossils and well-defined sedimentary structures. While several authors interpreted their genesis as evaporitic and/or diagenetic (Rouchy and Caruso, 2006), recently Guido et al. (2007) demonstrated that the CB carbonates are preserved in their original aragonitic mineralogical phase and are constituted of small crystals organized as peloids forming clots with an antigravitative fabric. The bright fluorescence indicates that peloidal micrite is rich in organic matter. The authors, using an organic matter study performed through Rock-Eval pyrolysis analyses, palynofacies observations and molecular-fossil recognition, demonstrated that carbonate precipitation was induced by bacterial ammonification of amino acids in aerobic conditions. Therefore these deposits are the results of biotic mineralization

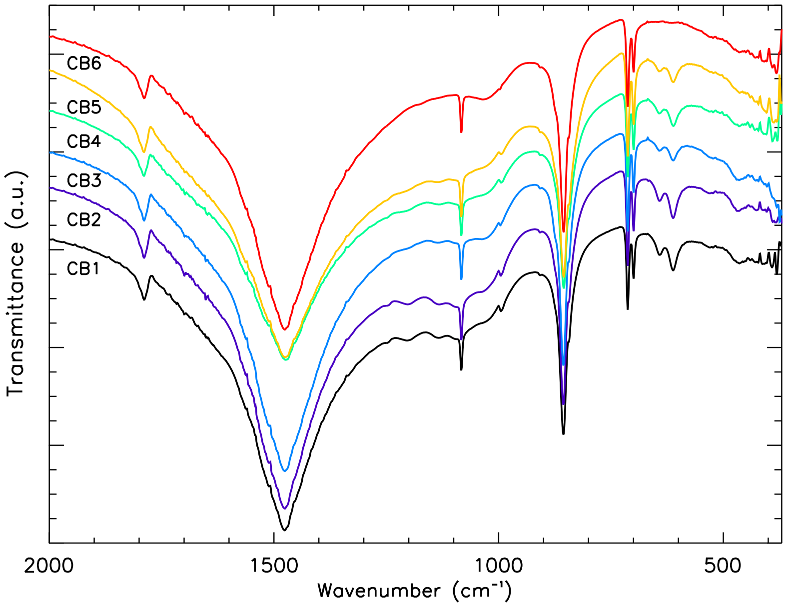

Fig. 2. Transmission spectra of the six samples (CB1 to CB6 from bottom to top) before heat processing. Spectra are arbitrarily scaled for clarity.

in a marine depositional scenario influenced by freshwater input rather than evaporitic concentration.

These problematic carbonates seem to represent a good sample to validate the applicability of the IR transmission spectroscopy in the discrimination between biotic and abiotic carbonates. The samples have been ground to obtain fine powders and then have been analysed by means of IR spectroscopy before (see Fig. 2) and after thermal processing at 485 °C for 3.5 hours.

As it can be clearly seen all the six transmission spectra before thermal processing exhibit the typical absorption bands of aragonite at 1476 cm^{-1} (6.8 μm), 1083 cm^{-1} (9.2 μm), 856 cm^{-1} (11.7 μm) and a double peak at 700 cm^{-1} (14.3 μm), characteristic of this mineral.

The presence in the spectra, either before and after thermal processing (Fig. 3), of other features in the 1200 - 1000 cm^{-1} and the doublet around 630 cm^{-1}, indicates the existence of some sulphate, most probably celestine ($SrSO_4$) as suggested also by our EDX (Energy Dispersive X-ray) analysis of the samples. Celestine is a mineral mostly found in sedimentary rocks often associated with carbonate marine sediments (Baker and Bloomer, 1988). The decreasing trend of the band depth of the two absorption features around 630 cm^{-1} from CB1 to CB5 (see Fig. 2) and its absence in the spectrum of CB6, may be linked to the diagenetic fluid composition. The diagenetic fluids, circulating in gypsum arenite layers, which lie below the Calcare di Base, are enriched with strontium and sulfates ions and consequently they improve the Celestine amount in the basal part of the carbonate beds.

Concerning the transmission spectra after the thermal processing, we find that all of them exhibit the same trend and, as an example, we show in Fig. 3 only the spectra of sample CB1 (see Fig. 1 for its location). In this case the position of the main bands in the spectra reveals that the transformation to calcite has occurred while the changes in the slope beyond

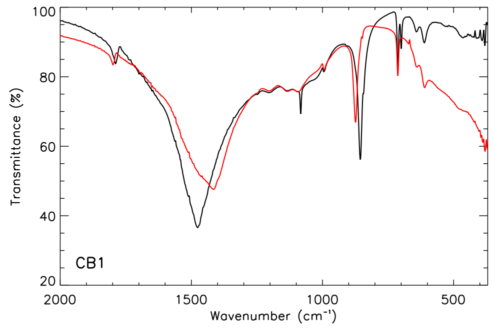

Fig. 3. IR spectra of sample CB1 before (black curve) and after (red curve) thermal processing for 3.5 hours at 485 °C.

700 cm^{-1} indicate that the conversion to CaO also began (Orofino et al., 2007). The evaluation of the D index, extensively discussed in previous papers, allows to discriminate between biotic and abiotic cabonates (for details see Orofino et al., 2007, 2009).

The D index estimates the variation of the spectral slope, beyond 700 cm^{-1}, between the spectra obtained before and after heating each sample at 485 °C. Due to the fact that the spectral slope is always steeper in the case of the processed sample, $D \leq 1$ for all the samples. We note that as D increases, the spectral slope of the processed sample becomes more similar to that of the unprocessed one, meaning that the thermal processing is less effective in the transformation of $CaCO_3$ into CaO.

The linear correlation found between the D index and the logarithm of the age of known biotic samples, allowed the creation of a useful graph which we named "biotic carbonate diagram" (Orofino et al., 2007, 2009).

The evaluation of the slope variation index D for the six samples under study and the knowledge of their geologic age, allow to include them in the plot of Fig. 4. The age of the samples (~ 6 Myr) has been inferred from their stratigraphic position while its uncertainty has been assumed equal to the half of the duration of the Messinian period, according to Gradstein et al. (2004). The lower D index value of the CB1 and CB4 samples could be linked to the carbonate purity. Guido et al. (2007) demonstrate that terrestrial organic matter and siliciclastic elements increase upward in both carbonate beds making less pure their upper parts.

As it can be seen in Fig. 4, the position of the points representing our CB samples clearly indicate a very likely biotic origin of the aragonite under analysis. This conclusion is in good agreement with that obtained by Guido et al. (2007) using a completely different approach based on complex geochemical techniques.

3. Conclusions

In the framework of the search for life on Mars, a method able to discriminate between biotic and abiotic origin of carbonate samples is certainly of valuable importance for the next generation of space missions to the planet.

In previous work (D'Elia et al., 2007; Orofino et al., 2007, 2009, 2010) we have developed a method to distinguish, by means of IR spectroscopy, abiotic calcium carbonate minerals from the corresponding biominerals in form of fresh shells and fossils found in different places and easily recognizable as of biotic origin. The IR spectroscopy of the sample after heating at 485 °C allows discriminating its origin, by means of the evaluation of the D index.

The linear correlation found between the D index and the logarithm of the age of known biotic samples, which we named "biotic carbonate diagram", can be used to:

a) discriminate between biotic and abiotic origin of other carbonate samples, both terrestrial and extraterrestrial;

b) individuate particular groups of carbonate fossils;

c) estimate the age of terrestrial samples of known biotic origin.

The evaluation of the age of the samples - point c) above - can be easily understood and applied. Concerning point b), the deviation from the linear trend has been already evidenced for a group of terrestrial fossils embedded in a layer of clay, with important implications in the search for biosignatures on Mars (Orofino et al., 2010).

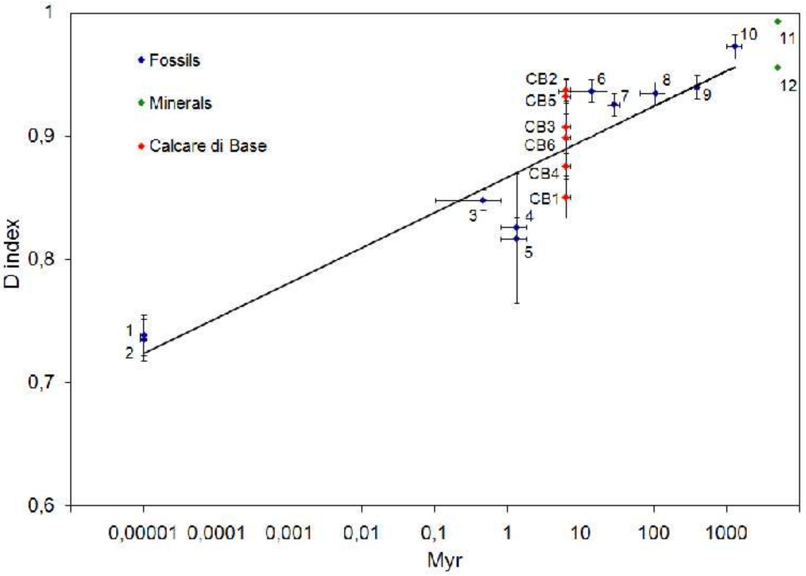

Fig. 4. Position of the six samples in the "biotic carbonate diagram". The D index for all the other samples (from ♯1 to ♯12) are those analysed by Orofino et al. (2009). The D values determined for minerals of abiotic origin (samples ♯11 and ♯12) have to be considered outside the chronological range.

As far as point a) is concerned, in this work we have applied our analysis to carbonate samples, in which there are no clear evidences of controlled or induced biomineralization, and we have shown that the method is really reliable and useful for discriminating between biotic and abiotic carbonates, even in the absence of well-defined fossil structures. Indeed, as it can be seen in Fig. 4, the mean position of these samples in the "biotic carbonate diagram" clearly indicates a very likely biotic origin of the aragonite samples under analysis. This is in agreement with the conclusion reported by Guido et al. (2007) who followed a completely different approach based on a complex set of sedimentary, petrographic, geochemical and biochemical analyses. It is worthwhile to note the relative simplicity of our method compared to the demanding geobiological investigations already applied and discussed by Guido et al. (2007).

Martian biotic carbonates could be detected by means of IR spectral analyses, making the "biotic carbonate diagram" a powerful tool for the search for life on Mars. This means that experimental projects designed as in-situ or sample-return analyses and based on IR spectroscopy, could be useful as diagnostic technique complementary and/or alternative to the differential thermal analysis already proposed for the same purpose (Cabane et al., 2004; Stalport et al., 2005, 2007). The choice of the more suitable procedure may obviously be dictated by several considerations and opportunities which are beyond the aim of the present work. In future we plan to increase the number of analysed fossils in order to improve the statistical significance of the "biotic carbonate diagram". The analysis of fossils older than those studied up to now, will be also useful in order to investigate the spectral reaction to heat processing of less preserved biological structures.

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