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The degree of biogenicity of micrites and terrestrial Mars analogues

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Abstract. A number of indications, as the past presence of water, a denser atmosphere and a mild climate on early Mars, suggest that environmental conditions favorable to the emergence of life must have been present on that planet in the first hundred million years, or even more recently. If life actually existed on Mars, biomarkers could be still preserved with some degree of degradation.
In previous laboratory works we have investigated the infrared spectral modifications induced by thermal processing on different carbonate samples, in the form of recent shells and fossils of different ages, whose biogenic origin is indisputable. The goal was to develop a method able to discriminate carbonate biogenic samples from their abiogenic counterparts. The method has been successfully applied to microbialites, i.e. bio-induced carbonates deposits, and particularly to stromatolites, the laminated fabric of microbialites, some of which can be ascribed among the oldest traces of biological activity known on Earth. This result is of valuable importance since such carbonates are linked to primitive living organisms which can be considered as good analogues for putative Martian life forms.
In this work we show that, studying different parts of the same carbonate rock sample, we are able to distinguish, on the base of the degree of biogenicity, the various micrite types (i.e. detrital vs autochthonous).

Key words. Exobiology – Mars – spectroscopy

1. Introduction

In upcoming years various space missions will investigate the habitability of Mars and the possibility of extinct or extant life on the planet.

On Earth, one of the most common approaches in the search for evidence of fossil life is the identification and characterization of biomarkers linked to organic compounds (Guido et al., 2007, 2011, 2013; Preston et al., 2010, 2011), although strongly limited by contaminations problems. These biomarkers can be preserved for billions of years, under favourable circumstances, and they provide very important insights into the early evolution of life on Earth (e. g. Summons et al., 1999; Brocks et al., 2003). If life was once present on Mars, biomarkers may still exist, even if great care has to be taken due to the possibility that they could originate from meteoritic organic compounds (Benner et al., 2000). In this context, we propose to consider the potential of biotic inorganic compounds (biominerals), since the probability of finding traces of biological activity 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 (Perry et al., 2007; Dupraz et al., 2009; Riding, 2011).

Calcium carbonate ($CaCO_3$) minerals are particularly interesting, because they can be produced either by abiotic processes or by biologically induced or controlled mineralization (Mann, 2001). Many living organisms on Earth, prokaryotes and eukaryotes, are able to biomineralize calcite or aragonite and actually the most primitive terrestrial evidence of life are biomineralized carbonates (Schopf, 1993; Westall et al., 2004). On the other hand, it is well known that carbonates are also produced by chemical precipitation following different processes not related to the presence of any life form (Wilkinson and Given, 1986).

By studying the different infrared spectral behaviour, after thermal processing of the samples at 485 °C, we showed that it is possible to distinguish abiotic calcium carbonate minerals (i.e. aragonite or calcite) from the corresponding biominerals (Orofino et al., 2007). We have then applied our method to different carbonate samples in form of fresh shells and fossils of different ages, skeletal remains of already complex terrestrial life forms.

Due to the relatively short period of time during which any hypothetical Martian life would have been able to appear and develop, it is commonly believed that only primitive forms, such as those found on early Earth, can be considered as good analogues for putative Martian life forms.

For this reason the method has been recently applied (Blanco et al., 2011, 2013) to microbialites, i.e. bio-induced carbonate deposits, and particularly to stromatolites, the laminated fabric of microbialites, well known to be typical examples of very primitive forms of life on Earth.

In this work we show that, by studying different parts of the same carbonate rock sample we are able to distinguish, on the base of the degree of biogenicity, the various micrite types, discriminating those due to the deposition of small calcite grains that underwent to transport phenomena (i.e, erosion and transport of pre-existing carbonate), named detrital or allochthonous micrite, from those deriving by biotic processes and directly associated to the organisms (i.e., in situ precipitation via bacterial mediation), named autochthonous micrite.

The results obtained are of valuable importance since such carbonates are linked to primitive living organisms that can be considered as good analogues for putative Martian life forms.

2. Methods and materials

2.1. Experimental method

On Earth the polymorphs of $CaCO_3$, aragonite and calcite, are produced by abiotic processes as well as by biological activity. According to Mackenzie (1970), when aragonite (a metastable phase of $CaCO_3$ frequently present in mollusc shells) undergoes heat treatment, an endothermic transformation into calcite (the stable state of $CaCO_3$) occurs. Then, after further heating, calcite decomposes into solid calcium oxide (CaO) and gaseous carbon dioxide (CO_2).

The latter transformation is complete at 800 - 1000 °C (Stalport et al., 2005, 2007), but the temperature at which it starts depends on the biotic or abiotic origin of the sample. In the case of recent biominerals, heating at 485 °C for 3.5 hours is sufficient to start altering their chemical and/or physical properties, while for minerals of abiotic origin higher temperatures are necessary. As described in previous works (see Orofino et al., 2007, 2009, for details) every mineral and biomineral has been spectroscopically analysed before (unprocessed samples) and after (processed samples) thermal processing at 485 °C. Analysing the spectroscopic results, it is evident that the thermal pro-

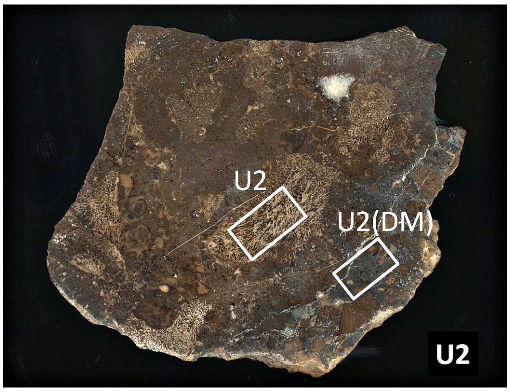


Fig. 1. The rock samples analyzed in this work.

cessing 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 "young" 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}, can be considered a discriminating factor. The investigation of old fossils revealed that the fossilization (diagenesis) process may lead to an almost complete alteration of the intimate structure to a level that very ancient fossils ($\geq$ 1 Ga) 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 effective in the transformation of $CaCO_3$ into CaO. The value of D can be seen as an index of fossil degradation, in the sense that D $\approx$ 1 implies the impossibility of discriminating between biotic and abiotic carbonate samples. This means that the thermal processing does not produce transformation of the calcium carbonate into CaO or, at the most, it produces only slight modifications.

2.2. Sample description and preparation

The term micrite, introduced by Folk (1959), is the abbreviation of "microcrystalline calcite" and is commonly used to describe very fine carbonate particles less than 4 μm in size. Particularly important is the distinction between biotic and abiotic micrite.

The observation at high magnification of micrite fabric in optical and electron microscopy can supply an initial contribution to understand the micrite origin. Unfortunately in some cases micrite do not show any diagnostic morphological features even if they are biotic in origin. For this reason the recognition of microbial activity is very difficult in ancient carbonates.

In this paper we analyzed three rock samples with microbial carbonates that developed, in time, in various palaeoecological conditions (see Fig. 1 and Table 1).

Table 1. Samples (see also Fig. 1) analyzed in this work

Sample	Description	Composition	Geologic period/epoch
S/L	Skeletal organism	Calcite	Upper Triassic, Carnian (229-217 Ma)
S/L(AM)	Automicrite	Calcite, silicates (traces)	Upper Triassic, Carnian (229-217 Ma)
S/L(DM)	Detrital micrite	Calcite, silicates (traces)	Upper Triassic, Carnian (229-217 Ma)
S1A	Skeletal organism	Calcite, Aragonite	Upper Triassic, Carnian (229-217 Ma)
S1A(DM)	Detrital micrite	Calcite, silicates (traces)	Upper Triassic, Carnian (229-217 Ma)
U2	Skeletal organism	Calcite	Middle Triassic, Ladinian (237-229 Ma)
U2(DM)	Detrital micrite	Calcite, silicates (traces)	Middle Triassic, Ladinian (237-229 Ma)

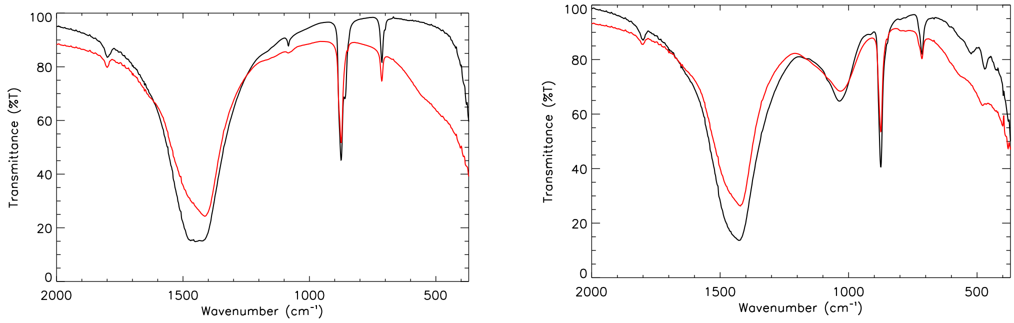
Two rock samples (S/L and S1A) are Upper Triassic in age (Upper Carnian, 229-217 Ma) and were collected from Picco di Vallandro (Prato Piazza, Western Dolomites, Italy). Skeletal organisms (Tubiphytes, skeletal cyanobacteria, sphinctozoan and inozoan sponges, etc.) represent a minor component of the rock (usually less than 40%). On the contrary the composition is dominated by the micritic fraction (about 60%), mainly represented by autochthonous micrite (automicrite), with subordinate amounts of micrite interpreted as detrital (allochthonous micrite) (Russo et al., 1991). The microbialites or autochthonous micrites, which may exhibit both dense microcrystalline (aphanitic) or peloidal microfabric, are sometimes organized in stromatolitic laminae or thrombolitic fabric. The organic-induced nature of microbialite was supposed on the base of micromorphological evidence and epifluorescence observations.

The U2 sample was collected in the basinal section which crops out at the base of Punta Grohmann mountain, belonging to the Sasso Piatto Massif, in the province of Bolzano, Italy. The Punta Grohmann section, 550 meters thick is one of the most studied basinal successions of the Ladinian-Carnian interval. The succession is characterized by the presence of displaced carbonate olistoliths (known in literature as "Cipit Boulders"), meter scale blocks exported into the basin from the eroded margins of the platform. The good preservation of these carbonate bodies is due to the very fine basinal sediments that engulfed them and prevented diagenetic processes. The sample, classified as "boundstone", is characterized by skeletal cyanobacteria (Cladogirvanella cipitensis), aggregated in centimetric-sized communities, which represent the main bioconstructors. Two type of micrite can be recognized: autochthonous (stromatolitic) and allochthonous (detrital micritic) (Russo et al., 1997). The first one, of biotic origin, is directly associated to the organisms and is organized in wrinkled laminations or very thin crusts that engulf sporadic skeletal grains. The second is due to the deposition of small calcite grains that underwent to transport phenomena. The Rare Earth Elements (REE) pattern reveals a marine distribution with the La, Ce, Gd and Y anomalies. The Heavy Rare Earth Elements enrichment (HREE) calculated as NdSN/YbSN is 0.84; the Y/Ho ratio is 53. These parameters indicate a well-oxygenated depositional environment (Mastandrea et al., 2010; Guido et al., 2011). Organic matter analyses and detailed recognition of the biomarkers revealed the presence of an extended series of hopanes, unsaturated fatty acids and double unsaturated aliphatic hydrocarbons. These data indicate the presence of cyanobacteria communities that induced the precipitation of the autochthonous stromatolitic micrite.

In order to study the two types of micritic components, we sampled and analyzed different parts of the same carbonate rock sample (see Fig. 1 and Table 1).

3. Results and discussion

As examples of spectra concerning the samples analyzeds in this work, we report in Fig. 2 the results pertaining to S/L, S/L autochthonous



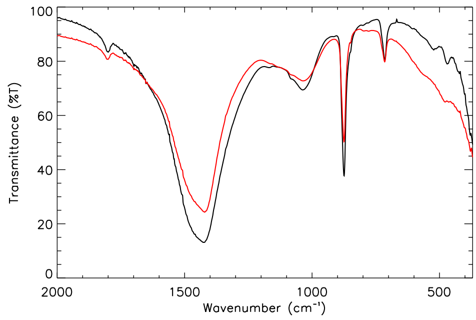


Fig. 2. Infrared spectra pertaining to (from top to bottom) S/L, S/L autochthonous micrite (S/L(AM)) and S/L detrital micrite (S/L(DM)), before (black curves) and after (red curves) thermal processing.

micrite (S/L(AM)) and S/L detrital micrite (S/L(DM)) (see image of the samples in Fig. 1). As it can be seen all the spectra show the typical absorption bands of calcite, before and after thermal processing, plus some traces of silicates clearly indicated by the features around 1050 cm^{-1} and 500 cm^{-1}. In addition, the transmittance below 800 cm^{-1} starts to decrease, due to the onset of the broad CaO band, centered at 330 cm^{-1}. Such change, however, is different for the three thermally processed samples.

Following the procedure described in section 2.1 (for details see Orofino et al., 2009) we have obtained the D index for all the samples under investigation in this work. The values, reported in what we called the "biotic carbonate diagram", are shown in Fig. 3 (red, green and blue squares) together with those (blue and black diamonds) obtained for the samples analyzed in previous works (see Orofino et al., 2009). The beginning and the end of each period/epoch are those established by the International Commission on Stratigraphy (ICS) devoted to the terrestrial stratigraphy on a global scale (Ogg et al., 2008). We have chosen the central age of the period the sample dates from, with an uncertainty equal to $\pm\,\Delta/2$ where Δ is the duration of each period. In those cases where the horizontal error bar is absent, it means that the error is contained within the physical size of the experimental dot. As far as the error on the D index is concerned, all the vertical error bars reported in Fig. 3 refer to the larger uncertainty between the statistical dispersion, derived from the error analysis of the various measurements performed on the same sample, and the instrumental accuracy of the transmittance spectra (typically 1%).

The linear trend shown in Fig. 3, obtained by considering only samples of known biotic origin as fresh shell and fossils (blue diamonds in Fig. 3), is reasonably well fitted by the function:

$$D = a \log t + b$$

where t is the age of the sample (in Ma), a = 0.0120 and b = 0.8645. The correlation coefficient is r ≈ 0.936 (Taylor, 1982).

This correlation implies that the recent fossils maintain the pre-diagenetic "fragility" (i.e. low resistance to thermal processing) of fresh biominerals, probably due to a less compact crystallization of biominerals and to their organic matter contents in comparison to abiotic calcium carbonates.

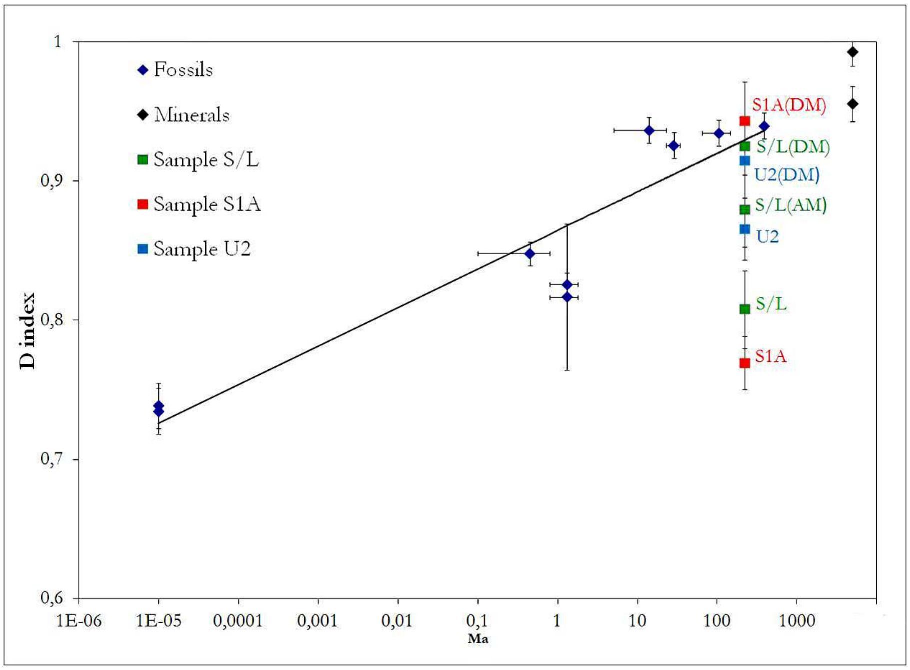


Fig. 3. Values of the D index plotted versus the age of the samples (in Ma) in logarithmic scale. Blue diamonds are the values for the samples of known biotic origin (fresh shells and fossils) analyzed by Orofino et al. (2009) and best fitted by the straight line. Red, green and blue squares refer to the samples analyzed in this work (see Fig. 1 and Table 1). The D values obtained for mineral abiotic calcite and aragonite (black diamonds) have to be considered outside the chronological range.

On the other hand for more ancient fossils the spectroscopic behaviour, after heat treatment, becomes increasingly similar to that of abiotic minerals and the D index is closer to 1. Therefore D could be seen as an index of degradation of the fossil, in the sense that D ≈ 1 implies the impossibility of discriminating between biotic and abiotic carbonate samples. The straight line represents therefore the place where the D index values of "normal" biotic carbonates fall as a function of the age, at least up to about 1 Ga in terrestrial environments. A deviation from this linear trend may indicate a particular situation and/or a different evolution of the biotic carbonate sample under analysis. In this context, we have also found that a group of terrestrial fossils embedded in clay-matrix exhibits values of D smaller than their coeval fossils found in other sedimentary successions. We confirm the interpretation of such behaviour as the result of a favourable condition for preserving their biomineral characteristics (Russo et al., 1991; Orofino et al., 2010). An interesting consequence of this result is that the phyllosilicates regions recently discovered on Mars (Bibring et al., 2006; Loizeau et al., 2007; Mustard et al., 2008; Wray et al., 2009) may represent very interesting environments that can provide conditions favourable to preserve evidence of biomarkers. Therefore they can be regarded as good candidate locations for biosignature detection. On the light of the above discussion and looking to the D values found for the samples analyzed in this work (see Fig. 1 and Table 1) we can conclude that:

a) all the samples contains biotic carbonates ($D < 1$);

b) the value of the index D, within the same rock sample, may be linked to the different preservation state of the material or to the type of component selected for the analyses;

c) the very compact texture of the autochthonous micrites and skeletal organisms (lower D), limited the transformation processes and preserved well the biogeochemical characteristics of the samples;

d) detrital micrite (higher D) show a lower biotic signal, in comparison to the autochthonous micrites and skeletal organisms, due to physical processes involved in its deposition. Actually the erosion and transport of preexisting carbonate promote the loss of the organic molecules preserved in the mineral fraction and foster the diagenetic processes.

This means that, by studying different parts of the same carbonate rock sample we are able to distinguish, on the base of the degree of biogenicity (different D values), the various kinds of the micrite component. The results obtained are of valuable importance since such carbonates are linked to primitive living organisms that can be considered as good analogues for putative Martian life forms.

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