The degree of biogenicity of micrites and terrestrial Mars analogues

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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, 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 minerals ($CaCO_3$) are particularly interesting, because they can be produced either by abiotic processes or by biologically induced or controlled mineralization (Mann, 2001).

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).

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.

At first we 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, then we analyzed in Blanco et al. (2011, 2013) microbialites, i.e. bio-induced carbonates deposits, and particularly 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.

2. Samples analyses and results

As described in previous works (see Orofino et al., (2007, 2009), for details) every minerals and biominerals have been spectroscopically analysed before (unprocessed samples) and after (processed samples) thermal processing at 485 °C. Analysing the spectroscopic results, it is possible to trace the alterations induced by the thermal processing and hence to link them to 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 process (diagenesis) may lead to an almost complete alteration of the intimate structure to a level that very ancient fossils behave spectroscopically like abiotic 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 (always $\leq$ 1) defined as the ratio between the spectral slope shown by a processed sample and that relative

Table 1
Samples 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	Upper Triassic, Carnian (229-217 Ma)
S/L(DM)	Detrital micrite	Calcite, silicates	Upper Triassic, Carnian (229-217 Ma)
S1A	Skeletal organism	Calcite, Aragonite	Upper Triassic, Carnian (229-217 Ma)
S1A(AM)	Automicrite	Calcite, silicates (traces)	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(AM)	Automicrite	Calcite, silicates (traces)	Middle Triassic, Ladinian (237-229 Ma)
U2(DM)	Detrital micrite	Calcite, silicates (traces)	Middle Triassic, Ladinian (237-229 Ma)

to the same sample before processing (Orofino et al., 2009). We observed that as D 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 at 485 °C. The value of D can be seen as an index of fossil degradation, in the sense that D ≈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.

As examples of spectra relative to the samples analyzed in this work (see Table 1), we report in Fig. 1 the results pertaining to (from top to bottom) skeletal grains (S1A), autochthonous micrite (S1A(AM)) and detrital micrite (S1A(DM)), before (black curves) and after (red curves) thermal processing. All the spectra show the typical absorption bands of calcite, before and after thermal processing plus, in some cases, traces of silicates clearly indicated by the features around 1050 cm^{-1} and 500 cm^{-1}. The bands due to silicates are particularly pronounced in the case of detrital micrite (S1A(DM)) indicating an expected higher content of these materials in the allochthonous fraction. Superimposed to calcite bands the spectrum of the unprocessed S1A sample (black curve in the upper panel of Fig. 1) shows also the absorption features at about 1084 cm^{-1}, 858 cm^{-1} and 700 cm^{-1}, due to the presence of aragonite (Salisbury et al., 1991; Blanco et al., 2013) in the S1A skeletal grains. As expected the aragonite features are strongly reduced after thermal processing. The most important change, however, is due to the decreased transmittance below 800 cm^{-1} due to the onset of the broad CaO band centered at 330 cm^{-1}. Such change, even if in different extent is present in all the three

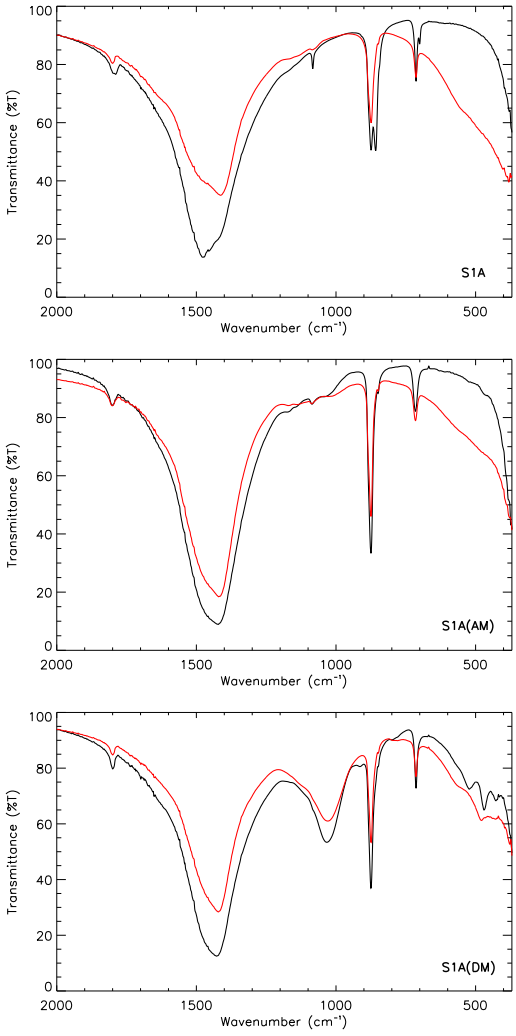

Figure 1. Infrared spectra pertaining to (from top to bottom) skeletal grains (S1A), autochthonous micrites (S1A(AM)) and detrital micrite (S1A(DM)), before (black curves) and after (red curves) thermal processing at 485 C.

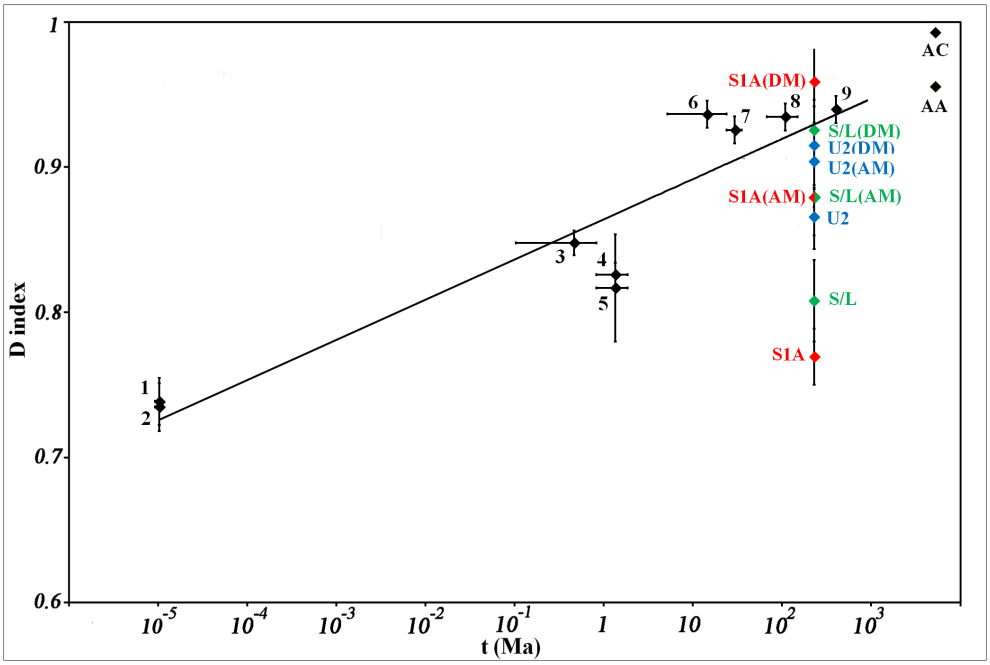

Figure 2. Values of the D index plotted versus the age of the samples (in Ma) in logarithmic scale. Black dots are the values for the samples of known biotic origin (recent shells and fossils) analyzed by Orofino et al. (2009) and best fitted by the straight line (see text). Red, green and blue diamonds refer to the samples analyzed in this work (see Table 1). The D values obtained for mineral abiotic calcite (AC) and aragonite (AA) have to be considered outside the chronological range (Orofino et al., 2009).

thermally processed samples.

Following the procedure described in Orofino et al. (2009), we have calculated the D index for all the samples under investigation (Table 1). The values are shown in the plot of Fig. 2 (red, green and blue diamonds) together with those obtained for the samples analysed in previous works (black dots from #1 to #9 plus abiotic mineral calcite AC, and abiotic mineral aragonite AA). 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 $\Delta/2$ where Δ is the duration of each period. In those cases where the horizontal error bar is absent, it means that it is contained within the physical size of the experimental dot. As far as the uncertainly on the D index is concerned, all the vertical error bars reported in Fig. 2 refer to the larger values 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%).

This correlation implies that the recent fossils maintain the pre-diagenetic "fragility" (i.e. low resistance to thermal processing) of recent biominerals, probably due to a less compact and regular crystallization of biominerals, possible linked to their organic matter contents, in comparison to abiotic calcium carbonates. 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 closer to 1. 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, as that of a group of terrestrial fossils embedded in a clay matrix (Orofino et al., 2010) showing the D values consistently smaller than their coeval fossils. Such behavior can be explained as the result of favourable conditions for preserving their biomineral characteristics (Russo et al., 1991; Orofino et al., 2010), and can have an interesting Martian counterpart in the phyllosilicates recently discovered on Mars (Bibring et al., 2006; Loizeau et al., 2007; Mustard et al., 2008; Wray et al., 2009), since they represent environments capable of providing favourable conditions to preserve evidence of biomarkers. The position in the diagram of the D values calculated for the samples studied in the present work (Table 1) clearly indicates their likely biogenic origin. The increasing values of D, i. e. D (skeletal grains) $<$ D (autochthonous micrites) $<$ D (detrital micrites) for all the three sets of samples,

is well correlated with the different amounts of organic matter evidenced by the epifluorescence UV images. This means that we can link the biogenicity or degree of biogenicity to the value of the index D. The different biogenicity may suggest also a different diagenetic history linked to the various types of carbonate components.

In conclution, by studying different parts of the same carbonate rock sample, we are able to distinguish the degree of biogenicity of 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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