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Microbialites vs detrital micrites: Degree of biogenicity, parameter suitable for Mars analogues

Armando Blanco^{a,*}, Marcella D'Elia^a, Vincenzo Orofino^a, Francesca Mancarella^a, Sergio Fonti^a, Adelaide Mastandrea^b, Adriano Guido^b, Fabio Tosti^b, Franco Russo^b

^a Department of Mathematics and Physics "Ennio De Giorgi", University of Salento, Lecce, Italy ^b Department of Biology, Ecology and Earth Science, University of Calabria, Cosenza, Italy

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ABSTRACT

In upcoming years several space missions will investigate the habitability of Mars and the possibility of extinct or extant life on the planet. 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 biogenic carbonate samples from their abiogenic counterparts. The method has been successfully applied to microbialites, i.e. bio-induced microcrystalline carbonate 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. In this work we show that, by applying our method to different parts of the same carbonate rock, we are able to discriminate the presence, nature and biogenicity of various micrite types (i.e. detrital vs autochthonous) and to distinguish them from the skeletal grains. To test our methodology we preliminarily used the epifluorescence technique to select on polished samples, skeletal grains, autochthonous and allochthonous micrites, each one characterized by different organic matter content. The results on the various components show that, applying the infrared spectral modifications induced by thermal processing, it is possible to determine the degree of biogenicity of the different carbonate samples. The results 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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1. Introduction

On Earth, one of the most common approaches in the search for evidence of microbial activities is the identification and characterization of biomarkers linked to organic compounds (Guido et al., 2007, 2011, 2013a, 2013b, 2013c; Preston and Genge, 2010, 2011; Preston et al., 2011), although strongly limited by contamination problems. These biomarkers can be preserved for billions of years, under favourable conditions, 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 of contamination by 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

* Correspondence to: Department of Mathematics and Physics "Ennio De Giorgi", University of Salento, C.P. 193, 73100 Lecce, Italy. Tel.: +39 832 297 468; fax: +39 832 297 505.

E-mail address: Armando.blanco@unisalento.it (A. Blanco).

http://dx.doi.org/10.1016/j.pss.2014.04.005 0032-0633/© 2014 Elsevier Ltd. All rights reserved. biological activity would certainly be higher if the search were 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 (CaCO₃) 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 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).

The increasing evidence of carbonates on Mars (Pollack et al., 1990; Bandfield et al., 2003; Ehlmann et al., 2008; Boynton et al., 2009; Palomba et al., 2009; Michalski and Niles, 2010; Morris et al., 2010; Carter and Poulet, 2012; Michalski et al., 2013), suggests that a number of locations may have existed where

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surface conditions would have been favourable for microbial habitability. In addition, the processes that deposited carbonate at the Phoenix landing site may have operated throughout the northern plains such that similar habitable locations could have been widespread (Sutter et al., 2012).

By analyzing 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 (CaCO₃ i.e. aragonite or calcite) from the corresponding biominerals (Orofino et al., 2007, 2009). We have then applied our method to different carbonate samples in the form of recent shells and fossils of different ages, skeletal remains of already complex terrestrial life forms. Due to the relatively short period of time (started around 4.0 Ga ago and lasted only a few hundred million years-Tian et al., 2009; Fassett and Head, 2011; Lammer et al., 2013) 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 carbonates deposits, and particularly to stromatolites, the laminated fabric of microbialites, well known to be typical examples of very primitive forms of life on Earth (Westall et al., 2004).

In this work we show that, studying different parts of the same rock sample we are able to differentiate the various origin of the fine carbonate fractions, namely the micrite types. The term micrite, introduced by Folk (1959), is the abbreviation of "microcrystalline calcite" and is commonly used to describe the particles less than 4 μ m in size. On the basis of the degree of biogenicity we were able to discriminate the micrites deriving from physical processes (i.e, erosion and transport of pre-existing carbonate), named detrital or allochthonous micrite, from those deriving by biotic processes (i.e., in situ precipitation via bacterial mediation), named autochthonous micrites or microbialites.

The different organic matter content of the three main components (skeletal grains, microbialites and detrital micrites), which characterize the carbonate rock under consideration, is related to the biogenicity of these compounds and can be used to prove the validity of the proposed method in the discrimination of biogenic samples from their abiogenic counterparts. The selection of the areas to be investigated, within the same sample, has been carried out according with the microfabric characteristics and their relative fluorescence under ultraviolet (UV) excitation. Actually, fluorescence reveal the presence and distribution of the organic matter so that the epifluorescence technique may be a valuable tool useful to select areas characterized by different degree of biogenicity to test our methodology (Russo et al., 1997; Guido et al., 2012b,2013a, 2013b; Mastandrea et al., 2011).

In the next section the main characteristics of the analyzed samples are described. In Section 3 the experimental measurements, consisting of epifluorescence observations and infrared (IR) spectroscopy, are fully described together with the essential features of the method. In Section 4 we report the experimental



Fig. 1. The rock sample S/L analyzed in this work. From left to right the panels show the selected areas within red and white rectangles (left panels), transmitted light photomicrographs (central panels), epiflurescences UV (right panels). From top to bottom the three panels refer to a skeletal carbonate of a coral (S/L, microbialites (S/L (AM)) and detrital micrites (S/L(DM)), respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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